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SEASONAL NUTRIENT DYNAMICS IN A SMALL-SCALE CONSTRUCTED  
WETLAND TREATING PRIMARY EFFLUENT WITH APPLICATIONS OF  
EFFLUENT REUSE IN BIOMASS PRODUCTION

By

Paul Thomas Miller

B.Sc. Radford University, Radford Va., 1996

Dissertation

presented in partial fulfillment

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Chemistry

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Approved by:

Dr. David A. Strobel, Dean  
Graduate School

Dr. Garon C. Smith, Chair  
Chemistry

Dr. E. Rosenberg  
Chemistry

Dr. Nigel D. Priestley  
Chemistry

Dr. Earle R. Adams  
Chemistry

Dr. Vicki J. Watson  
Environmental Studies

SEASONAL NUTRIENT DYNAMICS IN A SMALL-SCALE CONSTRUCTED  
WETLAND TREATING PRIMARY EFFLUENT WITH APPLICATIONS OF  
EFFLUENT REUSE IN BIOMASS PRODUCTION

Advisor: Garon C. Smith

Constructed wetlands have been investigated for use in the treatment of municipal wastewater. Species of nitrogen and phosphorus are the nutrients of focus and biochemical oxygen demand (BOD), total suspended solids (TSS) and fecal coliform are the pollutants. Prior work has focused on design concepts, plant effects on nutrient and pollutant treatment, and annualized treatment performance characteristics. This work builds upon published design concepts and wetland plant community and its function and investigates seasonal treatment performance and the kinetics of treatment performance for certain nutrients and pollutants during each season. Previous engineering based work has broadly suggested that first order kinetics govern the treatment chemistry of constructed wetlands. This work further investigates wetland chemistry by evaluating zero, first and second order kinetics for each season for certain nutrients and pollutants and compares regression analysis results between the orders. The results suggest that second order kinetics more closely describe the treatment kinetics realized. In addition, this work investigates an alternate function for constructed wetlands as a nutrient and pollutant buffer with the wetland effluent providing irrigation water for industrial crops. The industrial crops are then proposed to be utilized for energy production. Furthermore, a simple design model attempts to provide a rapid assessment of feasibility of constructed wetlands as a nutrient and pollutant buffer. The design model may be used by a municipality to quickly determine the feasibility of installing a wetland irrigation system as part of their overall wastewater treatment system. Finally, a simple mathematical correlation between a municipality's diesel fuel use and the projected size of a constructed wetland is presented.

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## 1.0 Introduction

The degradation and scarcity of freshwater is fast becoming a global concern (1). The threat persists as receiving bodies of water are degraded, demand for fresh or potable water continues to rise and supply dwindles (2). Increasingly, these supply, demand and quality concerns are not confined to villages of central Africa or Third World developing countries. Rural and urban American populations are both subject to similar issues with respect to ground and surface freshwater degradation from municipal waste water and sewage (3). Why is America, in particular smaller rural communities, at risk of degrading freshwater? In rural communities there is typically an insufficient tax base to support the infrastructure necessary for proper processing of municipal wastewater. In more urban communities, adequate sources of water are limited plus the quantity of nutrients released by conventional treatment overwhelms the capacity of receiving bodies to assimilate them. Both rural and urban America are at risk for ground and surface water degradation and the understanding of low-cost alternatives to large-scale centralized waste water treatment plants is critical for healthy policy decisions. In theory, and at times in practice, these low-cost alternatives do not apply an excessive tax burden on the municipality or community while still adhering to permit limits imposed by regulatory bodies.

Coupled with the receiving water degradation and diminishing fresh water resource problems are rising energy costs and availability issues. Critical public infrastructure services, such as solid and liquid waste collection systems, street cleaning, law enforcement, parks and recreation, water supply, snow removal, road repair and maintenance demand electrical energy, solid fuels, and liquid fuels in support of the

current expected level of public infrastructure, operation and maintenance (4,5). Diesel fuel consumption alone by the City of Missoula averages approximately 35,000 gallons per year (6). In 1956, M. King Hubbert, a petroleum geologist employed by Shell, published predictions that the domestic production of crude petroleum would follow a bell shaped curve and as a result would develop a peak (7). His work suggested that domestic production of crude petroleum would peak in the early 1970's. This event occurred in 1970 and the domestic production of crude petroleum has never recovered. In 1969, Hubbert began applying the same statistical principles that led to the prediction of domestic peak production to understand global peak production. Hubbert's predictions suggested that global reserves were at 2.013 trillion barrels and that global peak production would occur in the year 2000 (8). More recent work based on Hubbert's principles suggests a peak production in 2005 with total reserves of 2.1 trillion barrels (9). Additional independent work also suggests an impending global peak in petroleum production (10, 11, 12). These references do not suggest that the global supply of oil will be absolutely exhausted in the coming years; they merely suggest that global supply will decrease and global demand will increase resulting in both crude petroleum price spikes and price and supply volatility. With a considerable amount of the localized public service infrastructure reliant on petroleum-based energy sources, in particular diesel fuel, for operation and maintenance, these price spikes and cost exacerbates municipal budgeting problems and burdens as the energy costs exceed allocable tax based revenues.

A partial solution to the increasingly complex energy and wastewater management problem may be the re-use of partially treated wastewater effluent as nutrient-rich irrigation water. This understanding is predicated on an investigation of the

seasonal nutrient dynamics of a mesoscale constructed wetland system treating primary effluent from a municipal wastewater treatment plant. This work was conducted in an effort to understand if a particular low-cost alternative wastewater treatment system, a constructed wetland, could adhere to permit requirements while at the same time using the effluent to produce energy crops to convert into liquid biofuels for public services. The investigation focused on evaluating the constructed wetlands ability to treat biochemical oxygen demand (BOD), total suspended solids (TSS), ammonium ion concentration ( $\text{NH}_4^+$ ), total Kjeldahl nitrogen (TKN), ortho-phosphate (P), and fecal coliform (FC). The municipal wastewater treated was primary effluent. Samples were removed and evaluated over 3 years or 12 seasonal changes. The data generated were utilized to analyze pollutant and nutrient removal kinetics and develop seasonal concentration reduction constants for each of the criteria pollutants. This understanding was then utilized in determining the efficacy of a wetland treatment system for municipalities with similar wastewater, geographical and climatological characteristics with a particular application emphasis on rural communities with effluent re-use in industrial crop irrigation.

The crop of choice for irrigation was winter canola. Processing of this crop provides vegetable oil and protein meal. The vegetable oil can be converted into biodiesel. Biodiesel is a mono-alkyl ester derived from animal and vegetable-based triglycerides and has significant potential to be used in diesel engines (13, 14). The methyl ester of winter rapeseed, soybean oil, canola, sunflower, mustard and waste vegetable oil have all been found to be a potential and viable substitute for conventional petroleum based diesel fuel (15-20). The process of the conversion of triglycerides to

methyl or ethyl esters is known as transesterification which has been studied by an extensive body of investigators on a wide array of vegetable and animal fats (21, 22, 23).

Oil bearing plants and crops are cultivated around the world in a wide range of growing conditions (24). In the United States, particular emphasis has been placed on soybean oil as the raw material for biodiesel fuel manufacture. Soybeans are planted and harvested primarily for the protein content rather than the oil content or oil quality. However, soybeans require certain climatological characteristics and have limited cultivation potential outside of certain regions in the United States primarily the mid west and south east. Therefore identification and use of oilseed crops, other than soybeans, is critical for a broad-base re-use of treated wastewater for the cultivation of oil bearing industrial crops.

This dissertation provides background information on applications of constructed wetland treatment systems, gives an overview of performance characteristics from other similar studies and provides detailed discussion and evaluation of the seasonal performance characteristics of a constructed wetland. In addition, the work outlines a novel effluent re-use model that utilizes constructed wetlands for the production of industrial crops, with particular emphasis on oil seed crops, which may be harvested and processed into renewable diesel fuel.

## **2.0.0 Background**

### ***2.1.0 History and Timeline of Constructed Wetlands***

Prior to discussing constructed wetlands, an overview of natural wetlands is necessary. Natural wetlands are a vital part of the ecosystem and provide critical filtration mechanisms that clean both fresh and salt water. Unfortunately, prior to societies understanding of the full scope of their contribution to a balanced ecosystem, natural wetlands have long been thought of as a nuisance for urban or agricultural development. Historically, natural wetlands were filled in for the sake of real estate development for the advancement of private enterprise all in the name of progress. New understandings of the importance of these natural features have resulted in a suite of legal and regulatory protections at both the state and federal level which has slowed the wholesale destruction of natural wetlands, a necessary component in a healthy ecosystem. Coinciding with this evolution of understanding of the importance of wetlands as biological filters in the natural world was an understanding of their potential direct and applied beneficial use by mankind. Through advanced investigations of certain biogeochemical processes present in the natural wetland systems and the development of engineering techniques, mankind has begun to build and use “constructed” wetlands in the treatment of various kinds of wastewater from acid mine run-off to petroleum oil refinery wastewater streams to municipal wastewater.

The largest application and the topic of this discussion is the utilization of constructed wetlands for the treatment of municipal sewerage or wastewater. Historically, communities such as Lexington, MA; and Waldo, FL have discharged municipal wastewater into natural wetlands. As early as 1912, Lexington, MA began

discharging its municipal waste into the Great Meadows, a natural feature adjacent to the town and in 1939 Waldo, FL began the discharge of its municipal wastewater into a natural cyprus swamp (25). While the benefits of the inherent natural features of the wetlands were little known at this time, it is suspected that these natural wetland features provided a logical and convenient solution to civic leaders to solve a problem and it is apparent, given today's understanding of chemical processes within these systems, that some level of treatment undoubtedly occurred and provided a benefit to the community. Below is a table showing the evolution of the use of constructed wetlands treating wastewater.

| <b>Date</b>       | <b>Location</b>   | <b>Description</b>  |
|-------------------|-------------------|---|
| Pre-Historic      | Globally          | Natural filtration process  |
| 1912              | Lexington, MA     | Deliberate discharge of municipal waste to a natural wetland  |
| 1939              | Waldo, FL         | Deliberate discharge of municipal waste to a natural cyprus swamp   |
| 1950's            | Plon, Germany     | Treatment of chemical and dairy waste with bulrush planted wetlands   |
| 1960's            | Various locations | Systematic monitoring of natural wetlands receiving municipal waste water   |
| 1970's            | Ann Arbor, MI     | Specific focus on the design and engineering of "constructed" wetland for treatment of waste water                      |
| 1980's            | Various locations | Utilization of constructed wetlands for the treatment and or polishing of municipal wastewater                          |
| 1990's            | Various locations | Expanded scope of use of constructed wetlands for industrial waste streams, acid mine drainage and storm water run-off. |
| 1990's to present | Various locations | Experimental design, engineering, evaluation and optimization for enhanced constructed wetland treatment performance.   |

**Table 1. Constructed wetland development timeline.** Timeline of experimentation and utilization of constructed wetlands for treatment of waste water.

Expanding public interest in the environment and the passing of the Federal Water Pollution Control Act in 1972 (and as amended in 1977 as the Clean Water Act) initiated



a nation wide effort at understanding ground and surface water conditions and the implementation of regulatory control over municipalities and industries. Discharge to natural wetland features continued between 1981 and 1982. During this time it was determined that in the Southeast and Midwest (EPA Regions IV and V) there were approximately 324 discharges of municipal, industrial or other unknowns to swamps or wetlands (26). Forty nine percent (49%) of these discharges were considered municipal wastewater, twelve percent (12%) industrial wastewater and thirty eight percent (38%) were considered from other or unknown sources. However very little regulatory oversight was in place resulting in limited data collection regarding the biological or chemical activity within these wetlands. In certain cases, random and unorganized data were collected beginning as early as the late 1960s and early 1970s. Fortunately, these initial anecdotal and unsystematic evaluations of water quality conditions set the stage, in part, for understanding the utility of wetland ecosystems for remediation of wastewater streams.

European nations have contributed to the acceptance of constructed wetlands as a viable treatment option. Confidence building investigations were conducted at the Max Planck Institute in Plon, Germany by researchers Seidel and Kickuth in the early 1950's. This important work was prior to and laid a foundation for the significant research that was initiated in the United States in the early 1970's. From the late 1960's and into the mid-1970's Dr. Howard T. Odum of the University of Florida – Gainesville and a contingent of collaborators and graduate students focused on research related to the discharge of secondary municipal effluent to both salt marshes and natural cypress wetlands. At the same time that Odum was conducting his investigations, a similar effort

spearheaded by Robert H. Kadlec of the University of Michigan was underway. Kadlec's effort focused not on the use of existing natural wetland features as wastewater treatment options but on the design and engineering of constructed wetlands for wastewater treatment. Due to the geographical location of his investigations, the work has a special emphasis on cold weather performance. To his credit, Kadlec's work culminated in the commissioning of the Houghton Lake, MI project where a natural peat-land received summer flows of municipal wastewater. While not a constructed wetland, this particular project is still in operation today.

Brookhaven National Laboratory in New York was the first public institution to construct pilot scale wetland treatment systems in North America. In 1973 they designed a constructed wetland treatment system that utilized a meadow, a marsh and a pond configuration. Concurrent and prior to the results of Brookhaven effort Bellaire, MI initiated the discharge of "stabilized" municipal wastewater to a forest type wetland and Mountain View, CA constructed an 8.5 hectare (ha) constructed wetland with the goal of achieving both wastewater treatment and enhancing wildlife habitat.

In 1980, the community of Show Low, AZ constructed a wetland treatment system for treatment of municipal wastewater and enhancement of wildlife habitat and in 1984, Fremont, CA constructed a wetland marsh system to treat urban storm water runoff. In the same year, Incline Village, NV employed an innovative approach focused on a zero discharge or total assimilation wetland treatment system. In 1986, one of the most well known and documented projects was initiated in Arcata, CA where secondary municipal wastewater was discharged to a constructed wetland adjacent to Humboldt

Bay. This full scale treatment system followed four years of pilot scale research projects conducted at the City of Arcata Wastewater Treatment Plant (27).

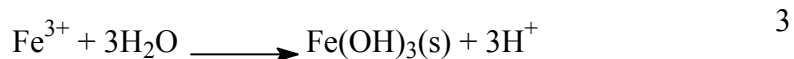
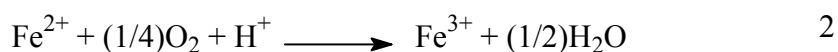
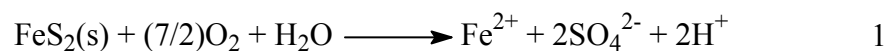
Constructed wetlands continue to be employed today as an option for communities to maintain or enhance their wastewater treatment capabilities. Of particular importance and what must be noted with all of the above projects is the population and volume of wastewater treated in each community. What must be understood is that constructed wetlands are better suited for smaller urban and rural communities that have sufficient open space as wetland systems demand substantial land resources for successful long-term performance. Constructed wetlands are not suitable for use by large communities with daily treatment volumes of greater than 1,000,000 gallons. Traditional and new technologies such as biological nutrient removal (BNR) are better suited for larger communities. As a comparison, BNR operations can treat volumes in excess of 50,000,000 gallons per day and are more appropriate for dense urban centers.

### ***2.2.0 Other Treatment Applications***

While the focus of this work is the treatment of municipal wastewater, it is instructive to understand that constructed wetlands are utilized in a variety of wastewater treatment applications. Each of these applications will be summarized in the following discussion.

### 2.2.1 Acid Mine Run-off

Wetlands have been utilized to mitigate the effects of acid mine run-off. The geochemical processes related to the development of acidic waters from coal mine run-off is represented below (28).

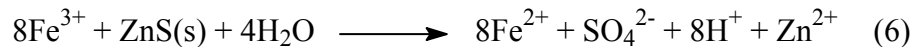
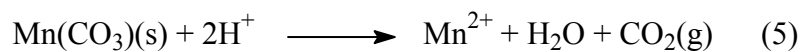


**Figure 1. Stoichiometric reactions of acid mine run-off**

Pyrite is the primary mineral behind the production of acid waters from coal mine operations. This oxidation based weathering process is triggered by the exposure of pyrite to oxygen. Hydrogen ions are produced upon the exposure of pyrite to oxygen based on the stoichiometric relationship that for every mole of pyrite oxidized, two moles of hydrogen ion are produced. This is the first release of  $\text{H}^+$  into the water. Lacking a suitable buffering mechanism, the resulting acidic aqueous environment in the presence of additional oxygen further oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (reaction 2). Iron (III), in the acidic aqueous environment precipitates out as ferric hydroxide generating three moles of hydrogen ion for every one mole of iron (III) oxidized, reducing the pH even more. Compounding the problem is the enhanced oxidation of pyrite in the presence of  $\text{Fe}^{3+}$  and water. This produces 16 moles of hydrogen ion for every one mole of pyrite oxidized providing for the proverbial “icing on the acid production cake”. The entire process is

further enhanced through microbial mediation of the conversion of ferrous iron to ferric iron.

If the problem were simply pH related, it could be managed. However, the acidic environment created by the oxidation of pyrite mobilizes other metals, in particular manganese (Mn). The production of ferric iron mobilizes zinc (Zn) while reducing ferric to ferrous and generating an additional eight moles of hydrogen ion (29). These irreversible processes are represented below.



**Figure 2. Mobilization of Mn and Zn.** With the oxidation of pyrite, Mn and Zn are mobilized.

Reaction 5 explains the presence of Mn in coal mine drainage. Metal mining operations with pyrite present in the ore body contribute to the mobilization of Zn, Cu, Cd, Pb and As in addition to the already present Fe, Mn and  $\text{SO}_4^{2-}$ . Interestingly enough is that mining operations without pyrite present generally do not have acidic water or a heavy metal mobilization issue. Based on this overview of the geochemical processes of acid mine drainage from both coal and metal operations it is apparent that the main focus for wetlands treating these systems is increasing the pH and precipitation and immobilization of metals.

The cost of immobilizing the metals and increasing the pH to more neutral values is of critical concern. Immobilization can be achieved potentially through:

- 1) The filtering of suspended or colloidal material and subsequent impoundment;

2) The assimilation or uptake of the metals into the plant structures such as roots and stems and adsorption in biological materials;

3) decay of biological material which may precipitate out metals through the generation of  $\text{NH}_3$  and  $\text{HCO}_3^-$ ; and

4) bacterial catalyzed precipitation (30).

Iron is generally stabilized as hematite ( $\text{Fe}_2\text{O}_3$ ), pyrite, or siderite ( $\text{FeCO}_3$ ) in peat bogs.

Trace elements are found as complexes of sulfides, oxides or carbonates. Based on these inorganic immobilized forms it appears that the biological contingency (plants, algae, etc.) within wetlands provides an intermediary wherein the subsequent decay of this biological material results in the re-mobilization of the problem metal in the inorganic form. The core focus, therefore, is the reversal of the above reactions using biological mediated processes. The approach is to establish reducing conditions with high concentrations of anaerobic bacteria. Properly designed constructed wetlands may provide these reducing conditions with high concentrations of anaerobic bacteria and thus an opportunity to immobilize metals. Anaerobic zones with sufficient levels of biomass will result in the formation of  $\text{NH}_3$  and  $\text{HCO}_3^-$ . The formation of  $\text{NH}_3$  and  $\text{HCO}_3^-$  causes an increase in pH which stimulates oxide precipitation of trace elements. It appears that metal uptake by plants is not the target mechanism, and that plants provide an environment and a surface for microbial growth which ultimately stimulate conditions for metal precipitation. In general, raising the pH precipitates out oxyhydroxides of iron and manganese in the aerobic zone. Also the following anaerobic conditions, creating an anoxic environment, limit the exposure of pyrite to oxygen thus reducing the chances of reactions 1-5 outlined above.

Real world applications for the treatment of acid mine run-off focus on initial aerobic conditions that precipitate iron hydroxides which are then followed by the establishment and maintenance of anaerobic conditions or reducing conditions so as not to re-release precipitated species. Other applications suggest an approach that couples precipitation of oxides with subsequent uptake of metals by algae (31). Overall, the body of work demonstrates that alternating aerobic and anaerobic conditions with stable microbial populations are a critical factor in the successful removal of metals (32).

While not an exacting solution to acid mine drainage problems and the resultant mobilization of metals, constructed wetlands do serve a role in mitigating the deleterious effects of exposure to oxygen of ore bodies rich in pyrite from historic mining operations.

### **2.2.2 Storm Water Runoff**

The urbanization of America has resulted in extensive areas of non-porous concrete and asphalt. The concrete and asphalt are used to facilitate vehicular transportation and parking for our automobile centric society. One result of this combination of vehicles and non-porous concrete and asphalt infrastructure is the deposition of petroleum products from leaky crankcases and transmission transfer cases as well as deposition of metals from brake pads and chlorinated organic compounds from herbicides, pesticides and fertilizers used in grounds keeping and landscaping applications. Depending on the configuration and design of the parking and transportation system, storm and rain events wash these materials into receiving waters such as lakes, ponds, wetlands and oceans and, depending on frequency and concentrations, may subsequently degrade the water quality. A proposed way to mitigate the negative effects of storm water run-off is the use of constructed wetlands as an

intermediary between the urban infrastructure and the natural receiving water.

Constructed wetlands have applications as a buffer between the contaminant rich urban run off and the natural water feature such as a river, lake or ocean; the ultimate receptor of the water. In addition, constructed wetlands provide a system by which storm waters can be “slowed down” to mitigate the effects of erosion on natural waterways and features.

Information on the ability of constructed wetlands and other man made features such as grass swales, sand filters and dry detention areas to treat storm water run-off is very limited (33, 34). This is the result of inconsistent methods used in the evaluation of performance ranging from sampling protocols, design information, and reporting methods. Thus, the ability to accurately predict the performance of constructed wetlands or wetland type features for treating storm water runoff is marginal at best. Therefore, the best way to review this particularly important application of constructed wetlands is to evaluate a case study.

The following will provide a brief overview of wetland and wetland features in the treatment of storm water runoff. In particular an overview of the Playa Vista project in Los Angeles will be discussed (35).

Playa Vista is a large commercial and residential development project in Los Angeles, CA. It is found just north of the Los Angeles International Airport bordering Marina del Rey and the Santa Monica Bay. Often, in densely populated urban projects, there exist numerous conflicting opinions on the objectives of storm water management and solutions to storm water problems and The Playa Vista project was no exception. The Playa Vista project provided an example of how an ecological solution could be



utilized to solve storm water run-off problems and address the concerns of the local stakeholders. The goal of the project was to reduce the amount of pollution being received by Santa Monica Bay, as well as providing additional natural habitat in an urbanized freshwater/saltwater interface. Important considerations in the overall design were the pollutant loads which, with statistical analysis, provided data as to the appropriate sizing of the treatment wetland complex. Tidal flushing was also incorporated into the design to ease the transition of storm water run-off into the Santa Monica Bay.

Prior to settlement of the region and the resulting urban sprawl that characterizes most of the Los Angeles basin there existed extensive fresh, salt and brackish marsh areas. These areas and the riparian ecosystem have essentially been removed, developed and replaced by large concrete flood control devices. Over the course of time, urban growth and development consumed the historical marsh area and it was all but destroyed. Roughly 1000 acres remained undeveloped in the Playa Vista area of the Los Angeles basin. However, the project area was effectively cut off from the tidal flows. In the 1970's development of commercial and residential infrastructure, by SUMMA Corporation, the heir of Howard Hughes, was opposed by community concerns based on the water quality issues and the desire for the historical marsh to be restored. Development attempts continued over the years but were unsuccessful due, in part, to traditional storm water management proposals that were not ecologically sound. In 1989 SUMMA Corporation sold a controlling interest in the project to Maguire-Thomas Partners (MTP). MTP initiated an ecological based design approach that addressed both their profit goals as well as the environmental goals of the community.

A number of water quality goals were developed. The goals were to:

- 1) Protect and enhance ground and surface water;
- 2) Satisfy the water treatment needs onsite and reduce the use of high quality drinking water for irrigation;
- 3) manage stormwater while maximizing habitat; and
- 4) employ innovative and proven technologies.

The goals were to have:

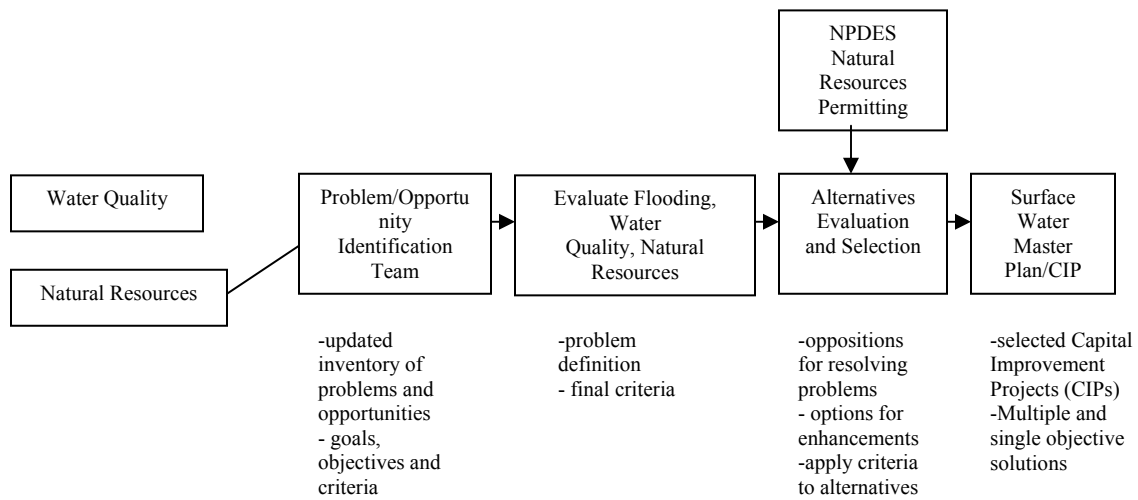
- 1) a “no net increase” in stormwater pollutant loads to Santa Monica Bay;
- 2) water re-use on site;
- 3) riparian open land; and
- 4) linkage with tidal waters.

Based on these goals and new design features, a pending lawsuit was settled between conflicting environmental and development concerns and the Playa Vista project was initiated.

The development site consisted of over 1,000 acres plus urban run-off or drainage from over 1,170 acres. It was recognized that, as development expanded, the water quality would change. In order to understand this change in storm water quality, a comprehensive statistically based storm water pollutant loadings model was developed and utilized to design the project. While not detailed in this discussion, in summary, the model incorporated GIS for land use understanding in the drainage area and utilized an extensive data set that was available from the Santa Monica Bay Restoration Project as well as from the US EPA and Federal Highway Administration. This data set provided information regarding the pollutant characteristics in the run off. Also, as part of NPDES

permit efforts in the L.A. basin, a data set was generated that included storm event sampling in 1996 and 1997 from 41 land use stations and 20 mass emission stations. These data sets revealed that copper and zinc were major pollutants in the storm water runoff as well as semi-volatile organics, organochlorine pesticides and PCBs, organophosphate pesticides, and chlorinated herbicides. The overall design basis for the wetland centered on heavy metals and total suspended solids (TSS) removal with source control measures used to reduce organics.

Traditional approaches to storm water run-off generally involve an “over-design” mentality based on a single annual storm event over a 24 hour period. Other traditional assumptions are made that have provided for property damage reduction but more damage to streams and receiving waters. These traditional assumptions have resulted in the excessive use of concrete to manage storm events often experienced in Southern California. In addition, the increase flows of fresh water to the salt marsh areas were a major concern in the Playa Vista project. These flows tend to lead to brackish water marshes which are considered less desirable non-natural habitat for Southern California. However, some freshwater events were needed for germination of desired native salt marsh wetland plant species, a goal to provide a natural native habitat. It was realized that a freshwater flood control marsh was necessary to reduce the impacts of large scale freshwater run-off into the salt water marsh. This integration presented a challenge to design engineers. A master planning process was utilized to facilitate and achieve the project goals. The following figure outlines that process.



**Figure 3. Stormwater master planning process.** An integrated stormwater master planning process description for communities and large scale developments. Adapted from Strecker, Woodward-Clyde (35).

This process generally produces a best management practice or BMP or otherwise known as the accepted and regulated solution. Factors included in the BMP selection process include:

- 1) Life cycle costs;
- 2) Regulatory requirements;
- 3) Flooding and pollutant concerns;
- 4) Implementability and Sustainability;
- 5) Environmental Impacts; and
- 6) Equitability, meaning are the measures fair within the community and for the

stakeholders.

Overall the Playa Vista project employed multiple BMPs to achieve the water quality goals. These included prevention measures such as street sweeping, car washing facilities, native landscaping reducing the need for irrigation and the use of herbicides, pesticides and fertilizers, community education, and community landscape maintenance.

Other measures included on-site water quality catch basins, survey of illicit or illegal dumping activities, introduction of a riparian corridor, pre-treatment areas in the wetland system and an actual freshwater wetland. The freshwater wetland was the largest and most complex component of the treatment train and also the most important. Design criteria for the freshwater wetland included:

- Capture and treat 90% of run-off
- Pre-treat runoff in specific zones prior to discharge to main wetland
- Create internal complexity to maximize contact area for stormwater
- Dense and diverse plant community
- Maximize wetlands habitat potential
- Reduce future maintenance burdens
- Safe and Attractive
- Avoid poor outcomes like invasive species proliferation

Estimated results of the project are outlined below.

| Receiving Water     | Concentration | Loading       |
|---------------------|---------------|---------------|
| To Ballona Channel: |               |               |
| TSS                 | 73% Reduction | 80% Reduction |
| Cu                  | 21% Reduction | 50% Reduction |
| To Marina del Rey   |               |               |
| TSS                 | 90% Reduction | 2% Increase   |
| Cu                  | 92% Reduction | 0% Increase   |

**Table 2. Playa Vista stormwater treatment results.** Estimated results of the urban stormwater runoff treatment project at Playa Vista in Los Angeles, CA. Adapted from Strecker, Woodward-Clyde, Portland, OR (35).

Overall, this project demonstrates that the use of constructed wetlands to manage storm water runoff is a viable option in large scale urban development projects. It, however, does take a significant level of planning and community and stakeholder involvement. This particular project suggests that storm water, if managed properly can be an asset to a community rather than a liability. This project provided a net benefit to

the receiving waters of Santa Monica Bay and to the owners of the property and residents of the new community.

### ***2.3.0 Municipal Wastewater Treatment***

The following is a review with respect to the use of surface flow (SF) constructed wetlands in the treatment of municipal wastewater. It is therefore prudent to provide a definition of a SF constructed wetland as one where the water surface is open to the atmosphere. The appearance of a SF wetland to the individual viewing it is akin to a pond with emergent and submergent vegetation. As previously discussed, wetlands have been utilized for nearly a century in the treatment of various kinds of wastewater. This background discussion is limited to recent peer reviewed articles that analyze various aspects regarding the use of SF constructed wetland treatment systems for municipal wastewater treatment.

Pioneers in the study of constructed wetlands for treating municipal wastewater quickly determined that biochemical oxygen demand (BOD), total suspended solids (TSS) and bacteria were readily treated to within permit limits. Hammer and Knight (36) initiated the detailed understanding of the ability of constructed wetlands to treat nutrients and, in particular, species of nitrogen (N) such as ammonia (as  $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ). In addition, Hammer and Knight attempted to correlate design features with treatment performance as studies indicated that wetlands had variable performance records with respect to species of N. Nitrification and denitrification require both aerobic and anaerobic conditions, ideally in that order. Both environments can be created by alternating shallow and deep water zones within the constructed wetland treatment system. Their goal was to develop a basis by which to predict the outflow of N from the

system based on influent concentrations. Their work suggested that predictions based on the loading of N (as kg N/ha-day) could be used to predict the effluent  $\text{NH}_4^+$  values. The results of their analysis suggest that combinations of shallow water zones with emergent vegetation followed by deep water zones with submergent vegetation with low  $\text{NH}_4^+$  loading rates can result in very low levels of  $\text{NH}_4^+$  in the effluent.

Crites published work suggesting specific design criteria for SF wetlands and subsurface flow wetlands (SSF) (37). This work also delineated the two types of treatment systems; those being SF and SSF systems with the following discussion limited to design criteria for SF systems. Crites determined that the process design criteria for SF systems are detention time, organic loading rate, water depth and aspect ratio. His work suggested a specific design criterion that is represented in the table below.

| Factor   | Typical Value |
|--|---------------|
| Detention Time in days (d)                               | 5 to 14       |
| Maximum BOD loading rate (kg/ha-day)                     | 80            |
| Water Depth in meters (m)                                | 0.1 – 0.5     |
| Hydraulic Loading Rate (mm/d)                            | 7 – 60        |
| Area requirement ( $\text{ha}/\text{m}^3 - \text{day}$ ) | 0.002 – 0.014 |
| Aspect Ratio   | 2:1 to 10:1   |
| Mosquito Control   | Required      |
| Vegetation Harvest Frequency, (yr)                       | 3 – 5         |

**Table 3. Surface flow design criteria.** Surface flow constructed wetland design criteria adopted from Crites, 1994.

Crites utilized a relationship that represented the effect on BOD removal and detention time (38). The Equation is shown below:

$$C_e/C_o = e^{-[k_T (86.68)t - \ln F]}$$

Where  $C_e$  is the effluent BOD concentration in mg/L,  $C_o$  is the influent BOD concentration in mg/L,  $k_T$  is the temperature dependent rate constant in  $d^{-1}$ ,  $t$  is the average detention time in days and  $F$  is the fraction of BOD that does not settle out in the first few meters of the constructed wetland.  $F$  can range from 0.8 for secondary effluents, to 0.75 for pond effluents and 0.52 for primary effluents. Therefore, as the quality of the water decreases, the fraction of BOD that does not settle in the first few meters increases. Crites published typical values for  $k_T$  on the order of  $0.0057 d^{-1}$  at  $20^{\circ}C$  where the relationship between temperature and the rate constant  $k$  is shown below:

$$k_T = k_{20} \times \theta^{(T-20)}$$

with  $k_T$  being the reaction rate constant at a temperature  $T$  in units of  $d^{-1}$ ,  $k_{20}$  is fixed at the typical value of  $0.0057 d^{-1}$ ,  $\theta$  known as the temperature correction factor is set at 1.06, and  $T$  is the average monthly water temperature in  $^{\circ}C$  (39). Combining these two equations the detention time can be calculated and with this value the area ( $A$ ) of the wetland can be determined by the following equation:

$$A = Q/d\Phi 10,000$$

Where  $Q$  is the average daily flow in  $m^3/d$ ,  $t$  is the detention time in days ( $d$ ), 10,000 is the conversion of  $m^2$  to ha,  $d$  is the depth of the SF wetland in meters ( $m$ ), and  $\Phi$  is the void ratio or the actual area that is occupied by water (38). Utilizing these equations, one can determine the size of wetland necessary to treat municipal wastewater with a certain loading rate and BOD concentration. Work by Crites did not specifically address other



criteria pollutants such as TSS or nutrient species of nitrogen (N) and phosphorus (P). Anecdotal suggestions were made for the treatment of N and P such as increasing the retention time and suggesting that the treatment of these criteria would be reduced at temperatures below 10°C and all but stop at temperatures below 4°C.

Crites did address the aspect ratio of a treatment wetland as an important parameter in the design of such systems. The goal in optimizing the length to width ratio is the avoidance of short circuiting of wastewater through the wetland. For large systems Crites suggests a minimum aspect ratio of 2:1. Crites addressed mosquito control as an essential provision in SF wetlands. The use of mosquito fish was suggested as well as the establishment of natural habitat for swallows and other predators. Vegetation harvesting was suggested as a way to maintain hydraulic conductivity and capacity, to promote active rather than passive growth of macrophytes, and as a way to manage mosquitoes. Crites suggested that harvesting the vegetation for nutrient removal is not practical and does not remove nutrients according to data presented by Reed (38).

In 2000 work out of the University of California at Berkeley by Bachand *et al.* attempted to develop an understanding of denitrification and the effects of temperature and vegetation in a surface flow wetland (40). The core reason behind this work was to understand the denitrification process in high quality nitrified waters in an effort to employ such lower cost passive treatment technology in an open space challenged urban setting. At the time of this research the role of plants in the denitrification process was relatively unknown. A goal of the research was to understand what plants enhance denitrification so as to properly design and optimize wetland treatment systems to be smaller and less expensive. The study evaluated three commonly utilized wetland plant

species including a bulrush (*Scurpis* spp.) and cattail (*Typha* spp.) and mixed stand of bulrush, cattail and grasses. The results of the work indicated that nitrate removal rates by wetland treatment systems with different types of vegetation varied significantly. Cattail planted wetlands demonstrated the ability to remove  $565 \text{ mg N m}^{-2} \text{ day}^{-1}$ , bulrush planted wetlands removed  $261 \text{ mg N m}^{-2} \text{ day}^{-1}$  and wetland planted with mixed vegetation removed  $832 \text{ mg N m}^{-2} \text{ day}^{-1}$ . This last data point highlights the benefits of vegetative diversity. From this work it was determined that bacterial denitrification, not plant uptake, was the driver behind the nitrogen removal.

Bachand also found that surface water temperature and organic carbon availability affected denitrification rates whereas surface water dissolved oxygen (DO) content and nitrogen concentrations did not. The study was unable to determine why different plant species affected the rates of nitrogen removal. The work presented results that suggest a diverse mixture of plants and grasses contributes to higher rates of denitrification in constructed wetland treatment systems; however, the reason behind this was unknown. This work addressed and provided insight into the processes associated with the denitrification of high quality nitrified water and the work did shed light on the temperature effects on denitrification. However, the temperatures under investigation ranged from a high of  $26^{\circ}\text{C}$  to a low of  $12^{\circ}\text{C}$  which does not provide any useful data for northern latitude or cold weather constructed wetlands. In addition, no rate data were as published with respect to BOD, COD, ammonia or phosphorus treatment or treatment capabilities.

Perkins *et al.* in 2000 published work relating to the investigation of SF constructed wetland's ability to remove enteric or intestinal bacteria (41). The work

focused on the tertiary bacterial treatment of municipal wastewater during the summer season between June and September. Bacteria of interest were fecal coliform and fecal streptococci. The work found that surface flow wetlands were efficient at removing both forms of bacteria with an 83-94% efficiency. However, the median fecal coliform concentrations in the final combined effluent from the four, in parallel, reed beds was 6000 CFU/100mL which is three times higher than the European Union directive of 2000 CFU/100mL. The work discussed that a number of factors influence the bacterial removal efficiency such as the flow rate, the die-off rate, the rate of removal by filtration and sedimentation, the rate of addition by birds and other wildlife or animal sources and the rate of predation. Flow rate appeared to be the biggest contributor to variability as the removal efficiencies decreased and at times the concentration of bacteria after storm or flood events in the final effluent was greater than the influent which was primarily due to the disruption of settled biomass.

Work at Arizona State University in 2000 by Gerke *et al.* attempted to develop a sequential model for the transformation of nitrogen receiving lagoon effluent in an arid climate and the potential for reuse of treated water (42). The sequential model in theory allows one to predict the concentration and species of nitrogen in the effluent based on the concentration and speciation of nitrogen in the influent. Coefficients of temperature and nitrogen species transformation rates for the model were successfully calibrated and verified with data from subsequent years. The sequential model focused on three processes those being ammonification, nitrification and denitrification.

In 2001 Coleman *et al.* investigated three wetland plant species native to Appalachia in small scale wetland treatment systems treating primary municipal

wastewater (43). The study involved subsurface flow wetlands with a regionally available gravel substrate at two gravel depths of 45 cm and 65 cm. In addition, 5 different planting treatments were investigated. Each species (*Juncius effusus*, *Scirpus validus* and *Typha latifolia*) was planted in a monoculture, as an equal mixture of the three plants and a control without vegetation. The wetland systems were loaded with 19L of wastewater per day with a frequency of 3 times per day. This was in an effort to simulate possible full scale wetland use in West Virginia. The influent and effluent water quality was measured with an average 70% reduction in TSS and BOD, a 55% reduction in TKN, ammonia and phosphate and a three order of magnitude drop in fecal coliform. The study determined that the depth of the gravel did not have an effect on the treatment performance. The depth of the gravel was found to influence the growth patterns of the *Scirpus* and *Typha* in addition, the gravel alone was found to provide treatment but the presence of vegetation enhanced the treatment performance. As expected the *Typha* outperformed the other two wetland plant species in growth within the monoculture systems and also out performed the other species in the mixed culture system. The core effort with this work was to understand how constructed wetland treatment systems may be able to be utilized in a decentralized manner in rural mountainous communities in West Virginia where centralized treatment plants present challenges. Traditional septic tank systems present challenges in this region because drain fields are subject to failure on steep rocky terrain or where groundwater and impermeable rock structures are near the surface. The constructed wetlands offer potential solutions where septic tanks have had problems and contributed to pooling effluent on the surface of the ground or where direct discharge to waterways is employed. This published work compared plant species

in their ability to treat primary effluent, work which had been conducted before, however not specific to West Virginian climatic conditions or geographical location. The study concluded that additional work should be conducted to further understand the role of these particular plants in constructed wetlands for the treatment of municipal wastewater. This study did not investigate or compare surface flow wetlands with sub-surface flow wetlands or any combination of the two. In addition, no kinetic or pollution reduction rates on an annual or seasonal basis were measured in this work leaving a large gap in the understanding of constructed wetlands applicability on a seasonal basis in the targeted geographical region.

Follow-up work by Hench *et al.*, reiterated the previous work conducted in West Virginia with additional focus on the fate of bacteria within the wetland systems (44). The work focused on the fate of fecal coliforms, enterococci, *Salmonella*, *Shigella*, *Yersinia*, and coliphage and measurable differences were found between the influent and effluent concentrations with these bacterial concerns. The planted systems showed the greatest microbial population reductions as compared to the systems that did not have vegetation. Also the results from this work suggested that over time the bacterial treatment performance decreased which generated questions regarding these types of systems as long term solutions for removal of bacterial pathogens from wastewater streams. An interesting aspect that this work evaluated, and one that is addressed in the work presented in this dissertation, is the treatment performance with respect to discharge permits. It was found that the discharge concentrations of contaminants did not meet permit regulations consistently for the receiving bodies of water. However, with this in mind, the results suggest that these types of systems may not be suitable for large scale

municipal treatment that must be permitted but may be suitable as a replacement strategy for non point source septic systems. The comparison in this literature cited was with respect to municipal discharge permits and it seems appropriate to compare “apples to apples” and look at the comparison and performance between constructed wetlands and traditional onsite septic drain field effluents to effectively evaluate constructed wetlands rural efficacy. Again, the work focused strictly on subsurface flow gravel bed constructed wetlands and did not look at surface flow systems or the integration of both.

A review article published by Werker *et al.* in 2002 gave an overview regarding the variability of treatment performance of wetlands for municipal wastewater in cold climates (45). The intent of the article was to highlight the growing need for these types of treatment systems and their applications in both urban and rural settings. The article suggests that the climate present in Canada poses unique and significant problems that are not currently being addressed. The article outlined key principles that need to be addressed which include the lack of a standardized approach to understanding wetland process mechanisms and a basis for comparing data within a system and between systems as they evolve over time. This work highlighted that it still remains difficult to know how well a chosen design is going to perform until it has been constructed and operated for some time. In addition, the notion was provided that these systems may not operate at theoretically designed efficiencies until the system has matured or in other words been allowed sufficient time for plant and root systems to develop. The work challenged the conventional wisdom of applying treatment kinetics and sizing the wetland area based on mathematical expressions and suggested that a deeper understanding and manipulation of the total ecology of the system is necessary to achieve long term predictable results using

minimal space and minimal capital resources. Due to the perception of risk and because of the wide range of treatment variability found in constructed wetlands in North America, Werker suggests research efforts should be focused on characterizing and quantifying the sources of variability in constructed wetland treatment systems in an attempt to help standardize and optimize design criteria. The author is quick to assume that surface flow (SF) wetlands do not hold utility in northern latitudes due to the extreme climatic conditions found during the winter months. The author fails to recognize that a properly designed SF system can remain operational by increasing the volume of water present in the system prior to the onset of winter. This increase in volume allows a layer of ice to form which, in combinations with snow and biomass cover, prevents a total “freezeup” of the system and allows water to flow. The paper presents a detailed review of the literature with respect to the removal of BOD, TSS, nitrogen and pathogens. Werker represents that activated sludge, the most common waste water treatment process in use today, has developed predictable performance by establishing a biomass concentration factor as the principle metric (46). The article also highlighted the understanding that wetland systems change both seasonally and with age and that this presents another “wildcard” that further challenges design and operations parameters and predictability in constructed wetland treatment systems. The work continues to suggest that wetland maturity, specifically with respect to root development and microbial activity, may be one way to correlate controlled laboratory experimental results with actual field investigations.

Rural communities generally use aerated lagoons for the treatment of municipal wastewater in an effort to reduce the BOD and TSS concentrations. Aerated lagoons

however provide limited treatment of nutrients. Cameron *et al.* in 2003 published work in an effort to refine the knowledge of the ability to treat municipal wastewater with constructed wetlands (47). This work attempted to clarify the treatment capacity of a constructed wetland receiving lagoon effluents over a period of one treatment season from May 19 to November 3, 2000. The system consisted of three surface flow cells followed by a phosphorus adsorption slag filter and completed with a vegetated filter. Bi-monthly water samples were taken at the inlet and outlet of each of the wetland features with comprehensive analysis of criteria pollutants including BOD, TKN, TSS, TP, ortho-PO<sub>4</sub> and fecal coliform. The results of this wetland treatment system are shown below.

| Pollutant<br>units | BOD<br>mg/L | TSS<br>mg/L | NH <sub>4</sub><br>mg/L | NO <sub>3</sub><br>mg/L | TKN<br>mg/L | TP<br>mg/L | o-PO <sub>4</sub><br>mg/L | FC<br>Count/100ml |
|--------------------|-------------|-------------|-------------------------|-------------------------|-------------|------------|---------------------------|-------------------|
| value in           | 3.62        | 82.67       | 0.11                    | 0.1                     | 1.67        | 0.33       | 0.18                      | 82.77             |
| Value out          | 2.38        | 6.18        | 0.05                    | N/A                     | 1.05        | 0.03       | 0.03                      | 39.38             |
| % removal          | 34          | 92.52       | 51.72                   | N/A                     | 37.3        | 89.89      | 81.82                     | 52.42             |

**Table 4. Wetland influent and effluent concentration in Ontario, Canada.** Single season influent and effluent concentrations for a constructed wetland treatment system from a lagoon pretreatment as well as percent removal in the Village of Alfred Ontario, Canada, population 1,100.

The aerated lagoon provides substantial pollutant removal and the concentrations of criteria pollutants are much lower as compared to the primary effluent. The percent removal of each of the pollutants is still very interesting as this constructed wetland could be considered a tertiary treatment step or have effluent polishing applications in rural community lagoon operations. Of particular note with this study was the successful use of slag filters in the removal of phosphorus. Up to 89% of the total phosphorus found in the lagoon effluent was removed. One drawback to this study is that data are taken only for one season of operation thus limiting the understanding of the treatment performance



over time and in cooler seasons. The work does highlight the utility of integrating multiple control strategies such as the surface flow system followed by the slag filters followed by a polishing vegetation bed. This is a fairly unique design that suggests diversification in treatment components is logical approach for constructed wetland design. .

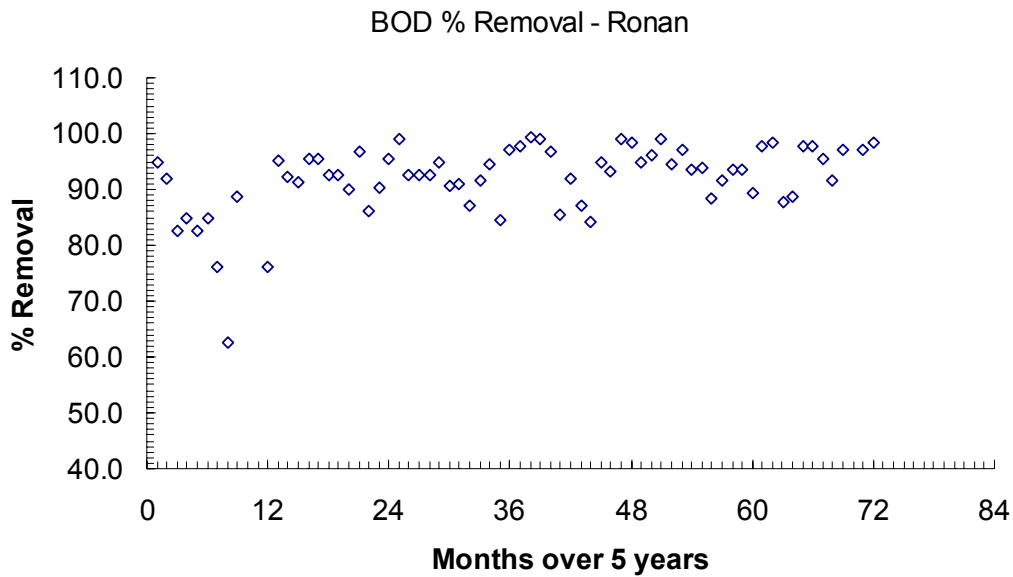
Interesting work published by Jing *et al.* in 2002 investigated the treatment of polluted river water (48). The pollutant of interest was ammonia and this work coupled a surface flow constructed wetland with a subsurface flow constructed wetland in an attempt to remediate the polluted river water. While not treating primary effluent, this work is instructive for its integration of two wetland treatment disciplines or philosophies those being the free surface wetland and subsurface wetland schools of thought. In addition, the concentrations of the ammonia varied seasonally and the effects of seasonally dependent temperature were examined at a constant hydraulic loading rate over two years of investigation. Removal constants (first order  $k_v$ ) were determined from this work as well as the respective temperature coefficients ( $\theta$ ). It was found that  $k_v$  increased with an increase in temperature however the mass removal rate decreased as the temperature increased which rendered the effect of temperature indeterminable. The hydraulic loading rate was kept constant, however, the mass loading rate varied due to changes in the concentration of ammonia in the river water. Overall, the paper determined that the seasonal variability in ammonia nitrogen removal rates was related to the mass loading rate.

A paper published by Ran *et al.* investigated the treatment of primary effluent in surface flow constructed wetland using duckweed (*lemna*) (49). The work explored cost

effective measures to treat primary domestic effluent (septic tank effluent) in a desert area environment. Due to the arid location of the work, a goal was to understand the re-use potential of the effluent from the system. The work determined the hydraulic residence time of 4.26 days, an average influent flow rate of 0.234 m<sup>3</sup>/d and a hydraulic load of 0.22 m/day was optimal. The work found good removal of TSS and BOD, with lower removal of nitrogen and negligible removal of phosphorus. Fecal coliform removal was high (>95%). This work also investigated the integration of the two types of systems: surface flow in combination with sub-surface flow systems. The use of duckweed was cited for its ease of removal for use as either a fertilizer or as animal fodder as the protein content of the duckweed approached 26%. The work was inconclusive and additional investigation was cited as necessary with respect to understanding the correlation between nutrient load and removal rate and the performance of the system during wintertime conditions.

#### ***2.4.0 Constructed Wetland Use in Montana***

Limited data are available on the viability of constructed wetland applications for the treatment of municipal waste water in Montana. A survey of the North American Wetland Treatment Database showed no published records of constructed wetlands performance in Montana. However, the longest running constructed wetland installed specifically for municipal wastewater treatment is found in Ronan, MT in the Flathead Valley. The monitoring of this constructed wetland treatment system was centered around biochemical oxygen demand (BOD) and total suspended solids (TSS). Below is plot showing the average removal percentage of BOD from this system.

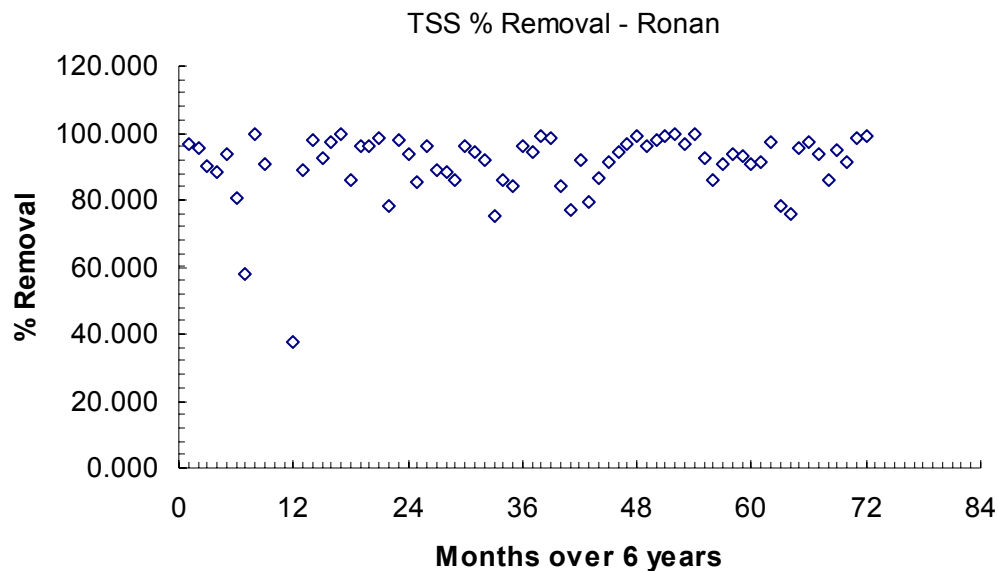


**Figure 4. BOD percent removal in Ronan, MT.** The percent removal of BOD at the Ronan treatment wetland over 5 years of data collection.

This plot indicates that the Ronan treatment wetland successfully reduces BOD concentrations between the influent and effluent to and from the wetland. The average percent decrease in BOD over the course of the data collection was  $91.9 \pm 6.4\%$ . The average influent concentration over the 72 months that these data were collected was  $179.42 \pm 68.2$  mg/L with the average effluent BOD concentration of  $13.06 \pm 10.01$  mg/L. No time course understanding of the BOD reduction was conducted so these data do not provide any indication on the performance with respect to a particular time frame. These data are consistent with published BOD performance and knowing that BOD treatment is generally a mechanical process it is not subject to seasonal temperature fluctuations. Wintertime months are concentrated around the multiples of twelve on the x axis in the above chart. By inspection of the plotted data, during the wintertime there appears to be no reduction in the treatment performance of BOD. Upon further analysis of the data, it appears that the effluent BOD concentration is independent of influent concentration as well as the season. The winter time average influent BOD concentration was  $169.11 \pm$

37.13 mg/L while the summer time average influent concentration was  $193.17 \pm 82.86$  mg/L. The winter and summer time effluent concentrations were  $11.89 \pm 6.40$  mg/L and  $10.91 \pm 12.01$  mg/L, respectively. This demonstrates that during the summer time the BOD levels were on the average approximately 12% greater than in the winter time. The effluent concentrations over the same seasonal comparison were essentially identical, with greater variability but not enough to violate operating permit limits of 30 mg/L of effluent BOD.

The other regulatory pollutant studied at Ronan was total suspended solid or TSS. Below is a plot of the percent removal of TSS over the course of the data collection.



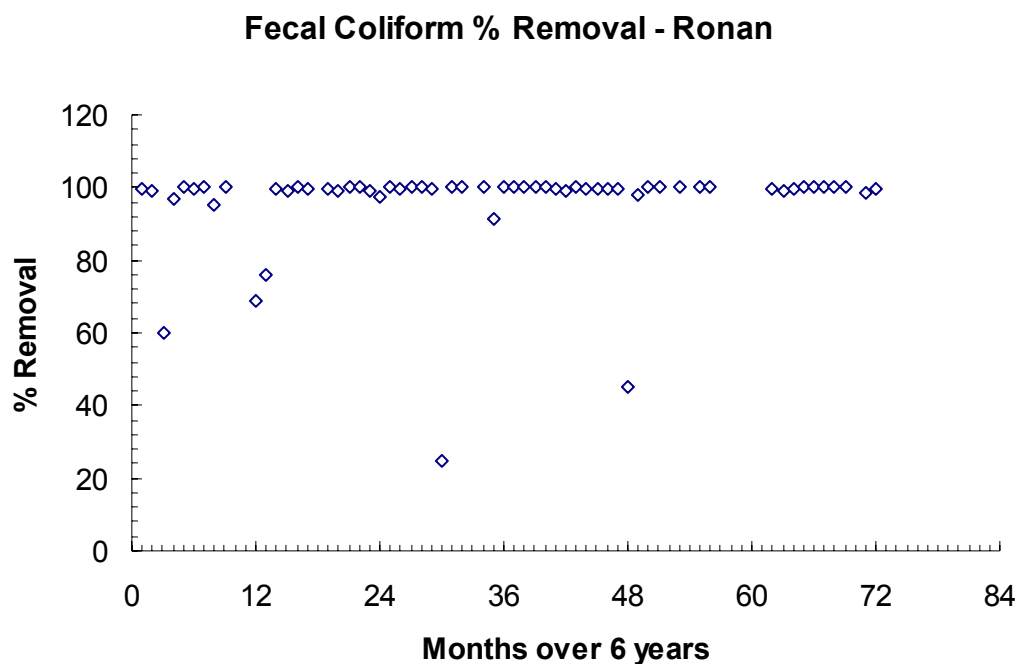
**Figure 5. TSS percent removal in Ronan, Montana.** Percent removal of TSS over the course of 6 years of data collection at the Ronan, MT constructed wetland.

Except for a few outliers with the first year of operation, the percent removal is quite good with an average percent removal of TSS slightly less than BOD at  $90.79 \pm 10.01\%$ .

The winter time TSS was slightly less at  $89.67 \pm 12.49\%$  as compared to the summer

time removal of  $92.58 \pm 8.03$ . As may be noted from these numbers, there is more variability in the winter with respect to TSS than in the summer season. Again, with these data no time course analysis was conducted so limited understanding of the actual daily performance of TSS through the wetland is realized. A potential reason for the lower levels of TSS removal during the winter season may have been a result of the slight viscosity increase of cold water as compared to warmer water found in the summer months.

Another area of treatment concern is fecal coliform. Fecal coliform provides an indication of the level of human feces remaining in the water as well as an indication of the overall general condition of the water body with respect to fecal matter generated by warm blooded animals. Below is a plot of the percent removal of fecal coliform over the course of the six year data collection.



**Figure 6. Fecal Coliform percent removal in Ronan, Montana.** These data were generated at the Ronan, MT constructed wetland facility over the course of 6 years.

The removal of fecal coliform was rather consistent except for five random events that occurred during the first four years of operation. It is not understood what the cause of these events was. It is suspected that spikes in the effluent concentration of fecal coliform could be due to uncontrollable natural events such as water fowl or migratory bird interaction with the wetland or it could possibly be related to a random decrease in the ability of the treatment wetland to handle the load of fecal matter to the system. The Flathead Valley of Montana is a flyway for migratory ducks and other water fowl and the wetland treatment system at Ronan, MT is of a free water surface design that provides open water surface upon which water fowl may land. Through communications with the facility operators, it is suspected that these random events are related to waterfowl and are not a result of lack of performance.

The overall percent removal of fecal coliform by the wetland treatment system was  $95.73 \pm 13.54\%$  with a slight decrease in the percent removal and greater variability of fecal coliform in the winter ( $93.27 \pm 17.42\%$ ) as compared to the summer ( $97.39 \pm 9.45\%$ ).

The data set for the Ronan, MT constructed wetland used for this discussion is found in the appendix.

### **3.0.0 Feasibility in Missoula**

The following is a feasibility study submitted to the City of Missoula – Waste Water Division. The intent of this study was to help City managers and the Superintendent of the Missoula waste water treatment plant understand constructed wetlands as a possible option for wastewater treatment at the City of Missoula waste water treatment plant. The report was submitted in July of 2003.

#### **Report Summary**

Constructed wetlands have provided a natural, low-energy, treatment option for treatment of wastewaters from industrial, agricultural, municipal and mining sources. This report addresses constructed wetlands as a treatment option that can be integrated into the existing wastewater treatment process to help manage potential permit-violating discharge events.

While having no substantial direct revenue generating potential, constructed wetlands do have the potential to provide a diverse habitat for animal and plant communities as well as providing aesthetic benefits including land and open space conservation. Constructed wetlands as a treatment application at the City of Missoula waste water treatment plant (WWTP) would be utilized most effectively from late March to early November to minimize direct discharge of potentially nutrient rich secondary effluent to the Clark Fork River. In addition, with proper design and management a portion of these wetlands could treat primary effluent during peak flow periods. The land requirements for direct discharge of all primary effluent to constructed wetlands exceeds the realistic acreage currently owned by the City of Missoula and acreage available

directly adjacent to the WWTP. Considering this, the appropriate use of constructed wetlands at the WWTP is for tertiary polishing of secondary effluent that may not be meeting permit discharge limits or the treatment of primary effluent in support of the main process. In this latter case, the constructed wetland may, during large flow events, perform intermittent treatment of primary effluent to reduce the strain on the existing treatment plant operations. In addition, experimentation with and demonstration of constructed wetlands and integrated natural treatment systems should be continued as a way to mitigate basin wide effluent impacts in the Clark Fork watershed. This experimentation and demonstration will continue to establish local expertise and be a resource upon which regional communities can access information from which to better determine the most cost effective and appropriate treatment method for their community.

Average cost for surface flow constructed wetlands is \$26,557 per acre (25, 39). The major costs with surface flow wetlands are with earthwork (25). Subsurface flow wetlands cost about eight times more than surface flow wetlands. The average cost for subsurface flow wetlands is \$218,752 per acre (25). Major costs associated with subsurface flow wetlands are with fill material (~\$7 per ton locally in Missoula).

Pilot scale treatment wetland studies conducted at the City of Missoula wastewater treatment plant have demonstrated favorable results. Preliminary experimentation has shown that a loading rate of 26 kg TN/ha-day reduced the concentration of TN 83% in a seven-day treatment cycle. These data are based on only one year of wetland operation during summer time conditions, a time period in which biomass is very productive and in theory, a wetland system achieves it highest level of performance. Therefore, the data do not represent long term performance characteristics



or seasonal characteristics and additional work needs to be conducted to understand the localized long-term and seasonal performance characteristics.

It is understood that the WWTP plant is interested in reducing its discharge of effluent and constructed wetlands may provide a reduction in the total amount of discharge from the WWTP and provide additional reductions in nutrient rich effluent discharge during the summer season and therefore reduce the nutrient impacts on the Clark Fork Watershed during this sensitive and productive time of the year.

In summary, sufficient land is not available for constructed wetlands around and adjacent to the WWTP to treat all of the wastewater generated by the city. However, sufficient land does exist that would enable intermittent or seasonal use of constructed wetlands during peak flow or at times when existing processes are not achieving discharge permit limits.

### ***3.1.0 Feasibility Study Background***

The City of Missoula is a point source for discharge of nutrients to the Clark Fork River (53). In addition, the population growth of Missoula, and additional residential sewer connections have led to the need for an upgrade to the current treatment facility. The upgrade, due to the volume of water being treated, is appropriately utilizing biological nutrient removal (BNR) as the treatment technology. However, there is interest in extending and enhancing the treatment capacity of the new plant utilizing integrated natural treatment systems such as constructed wetlands and hybrid poplars (54).

Constructed wetlands and hybrid poplars are the treatment options that are being assessed to enhance the treatment capacity of the WWTP and reduce the discharge of

nutrients to the Clark Fork River. Feasibility is being conducted targeting the intermittent or seasonal use of these systems at the WWTP as a way to reduce the total discharge of nutrients to the Clark Fork. In addition, the implementation of these treatment options may serve as a resource and model for smaller communities in the Clark Fork drainage and other watersheds in the region. By initiating the use of constructed wetlands and hybrid poplars to treat a designated capacity of secondary or primary effluent, the neighboring communities under pressure to upgrade existing facilities may utilize the information and data generated by the WWTP and this research. Missoula's leadership role in application of these "low tech" solutions and the utilization of the experimental data by other communities in the watershed may minimize the planning costs, reduce neighboring community's impact on the water shed, and enhance those communities' municipal treatment capabilities.

### ***3.2.0 Constructed Wetlands: An Overview***

#### **3.2.1 What are Constructed Wetlands?**

Constructed Wetlands are man made wetlands. They can be built where wetlands once existed or can be built in a "green field", where no natural wetlands existed. Wetlands have a higher rate of biological activity as compared to other ecosystems. Mimicing this natural feature in a "constructed" wetland enables these wetlands to breakdown, convert, or transform pollutants commonly found in conventional wastewater to harmless byproducts and essential nutrients for additional biological growth (25).

Constructed wetlands are generally built to provide some type of service in the realm of wastewater treatment or effluent polishing. In general, the pollutants in a wastewater stream are identified and matched against discharge permit limits and then a

specific conceptual design of a constructed wetlands is executed that will treat the particular type of wastewater stream (50). Constructed wetlands have been used to treat wastewater from storm water run-off, industrial discharge, agricultural wastes, municipal wastes, and mine drainage (38). Each of these applications has demonstrated a large amount of success. They are all, however, geographically and climatologically unique.

Constructed wetlands consist of both surface flow (SF) and subsurface flow (SSF) wetlands. The SF wetlands consist of a cell or cells having shallow depth (0.10 - 0.75 m) plant filled zones alternating with deep open water zones (up to 1 m) with submergent plants. Subsurface flow wetlands are generally an excavation filled with gravel and planted with wetland vegetation (51). Each type of constructed wetland consists of both inlet and outlet structures. Advanced constructed wetland designs include vertical flow through integrated surface and subsurface wetlands, effluent recycle, and reciprocating subsurface flow where cells are rapidly drained and filled (52).

Secondary services or ancillary benefits provided by constructed wetlands are generally aesthetic. Constructed wetlands provide habitat for a diverse community of plants and animals, help preserve open space, and most importantly provide educational opportunities and additional community awareness regarding the use fresh water and discharge of waste water. One of the challenges of the 21<sup>st</sup> century is the education of the public regarding the usage of freshwater and the life cycle of municipal water through the public works. With focused education and public awareness within communities the Missoula WWTP might realize a reduction in pollutant load and flow to the WWTP thus reducing operating and cost associated with construction intensive upgrades. Constructed wetlands may not treat all the municipal wastewater from Missoula. However, use of this

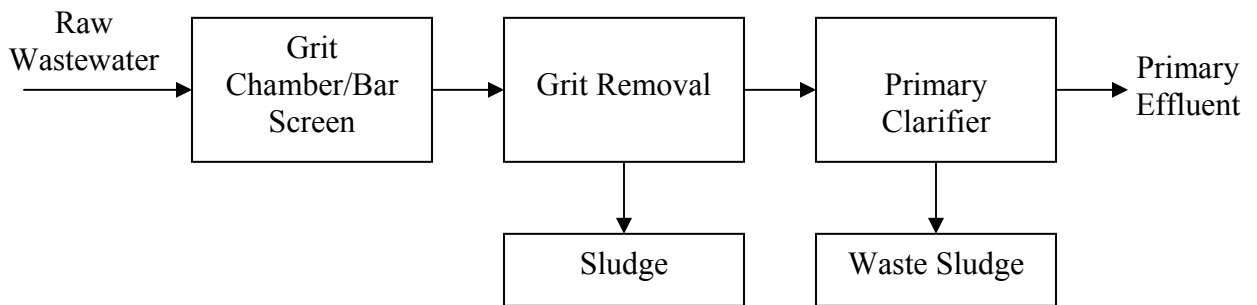
technology in some facet within the community or within the Clark Fork watershed may enable the public to recognize the municipal water life cycle and potentially reduce their discharge of harmful recalcitrant wastes into the municipal treatment system.

### ***3.3.0 Constructed Wetland Applications in Missoula***

Constructed wetlands have been considered by the City of Missoula as an alternate treatment option for management of nutrient and pollutant concentrations discharged from facility. The feasibility of the such a wetland system is discussed in this section. The feasibility is focused on treating primary effluent from at the Missoula wastewater treatment plant. Background data are provided on the concentrations of various pollutants in the primary effluent and preliminary data are provided from the author's experience with treating this primary effluent in an experimental scale constructed wetland treatment system. In addition, the sizing and cost of a constructed wetland is provided for both total and partial treatment of the primary effluent.

#### **3.3.1 Missoula Primary Effluent Data**

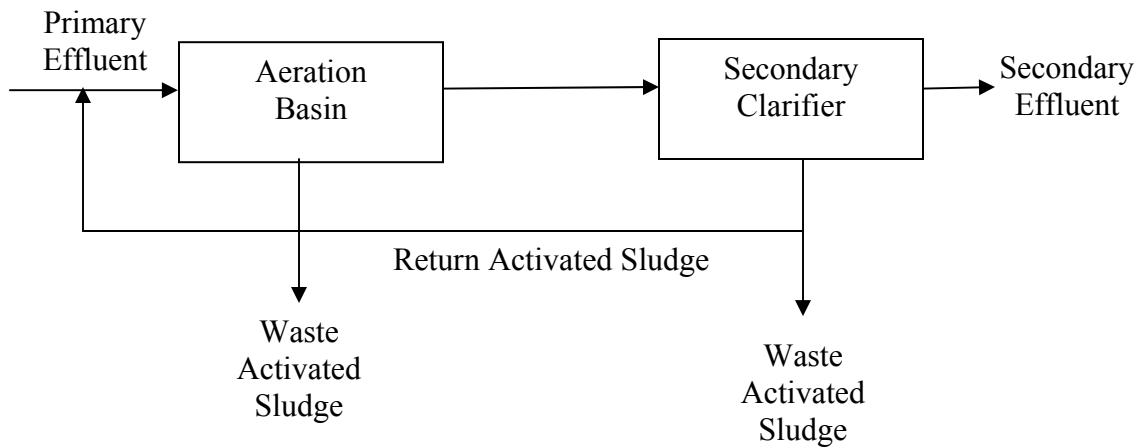
Primary effluent is wastewater that has passed through an initial gravity induced settling. With the configuration of the wastewater treatment plant, the primary effluent treatment stage is located after the head works and grit chamber and before the secondary activated sludge treatment system. Below is a diagram of a typical primary effluent treatment process flow.



**Figure 7. Typical treatment process for primary effluent.**

As may be noted from the diagram, the raw wastewater enters the wastewater treatment plant in an area known as the head works. Located in the head works is a grit chamber and or bar screen that removes large solid objects. Included in the process is a grit removal step that provides additional screening and finer grit material removal which generates a sludge that is pumped to an anaerobic digester (not shown). The wastewater is then introduced to the primary clarifier. Under gravity, heavier weight suspended material settles out as a sludge and again is pumped to the anaerobic digester. The resultant supernatant from the primary clarifier is called primary effluent. This is the level of wastewater pretreatment conducted prior to introduction to the experimental constructed wetland.

The primary effluent, in the treatment process at the Missoula wastewater treatment plant, is then further treated by an activated sludge process where the nutrients, nitrogen and to an extent phosphorus, are consumed by suspended bacteria in a mixed and aerated basin. Below is a diagram showing this step of the treatment process.



**Figure 8. Typical treatment process for activated sludge.** This is the process which is employed at the Missoula wastewater treatment plant.

In this process primary wastewater is introduced to an aerated basin which contains activated sludge. Activated sludge is essentially suspended microorganisms specifically suited to consume large amounts of nutrients. As the name implies the aerated basin is continuously mixed using large volume air pumps. Rapid introduction of air into the basin provides both mixing and dissolved oxygen for microbial growth. This aerated liquid is then diverted to a secondary clarifier for settling. A metered portion of the settled material (activated sludge), depending on the process conditions, is recycled back to the incoming primary effluent stream to charge the aeration basin. The remaining activated sludge is diverted to the anaerobic digester for treatment prior to dewatering and composting.

At the City of Missoula Waste Water Treatment Plant (WWTP) the largest concern is the discharge of nutrients after the secondary treatment process (in the form of

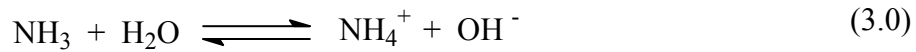
ammonia, nitrate/nitrite, and ortho-phosphorus) to the Clark Fork River (88). This discharge, especially in the summer months, provides a nutrient source for the production of algae whose decay results in a depletion of oxygen in the water column (89). Constructed wetlands offer a low cost alternative to retain the nutrient rich primary effluent in a “natural” system for treatment and re-use or constructed wetlands may be used after the secondary clarify to provide “tertiary” treatment of nutrient rich water or an additional buffer prior to discharge to the Clark Fork River. Conceptually, with the diversion of the WWTP effluent to a constructed wetland, the Clark Fork is buffered by a natural system which consumes and treats these nutrients. In addition, the treatment wetland can be designed and landscaped to blend in with the existing terrain to minimize the visual impact of such a system. Furthermore, the nutrients that are not consumed by the wetland, especially in the case concerning the treatment of primary effluent, may be re-used in the irrigation of revenue generating industrial crops.

The focus of this feasibility study is the treatment of primary effluent with a constructed wetland system. The Missoula waste water treatment plant samples their primary effluent as a way of monitoring this first stage of the treatment process. Included below are data for the primary effluent at the Missoula wastewater treatment plant. These data were generated between January 1999 through the end of May 2003. This period encompassed four winter seasons and three summer seasons.

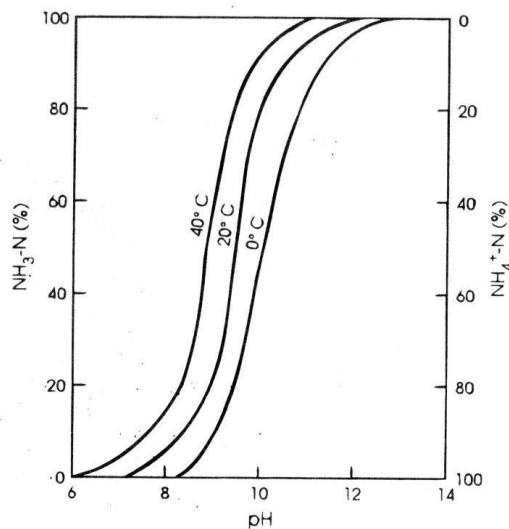
### **Ammonia ( $\text{NH}_4^+$ )**

Ammonia (as  $\text{NH}_4^+$ ) is a nitrogen (N) compound and is a concern because of its role as a precursor to oxidized N compounds such as nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ). Nitrogen found in ammonia is in the chemically reduced oxidation state of -3.

Depending on the water temperature and the pH, ammonia can be un-ionized or found in its ionized form known as the ammonium ion ( $\text{NH}_4^+$ ). Below is a simple chemical equilibrium showing the two forms of ammonia.



The following figure demonstrates the changes in speciation of ammonia depending on the pH and temperature. The primary effluent averages between neutral and slightly basic (7.0 – 7.5). Knowing this and that the temperature of the primary effluent averages between 13°C and 18°C, one can see that the ionized form of ammonia is the dominant species. It is not until a pH of greater than 8 with certain temperature conditions that the un-ionized ammonia species dominates.



**Figure 9. Conditions for un-ionized ammonia.** This plot demonstrates the effect of pH and water temperature on the fraction of ammonia in the ionized and unionized forms (25).

Nitrogen compounds in primary effluent, as may be noted from the table below and subsequent discussions are largely present as ammonium ion. As wastewater travels



through the municipal collection system, to the headworks and ultimately the primary clarifier there exists very little oxygen interaction. In addition, during the transport through the municipal infrastructure, the oxygen that is introduced through turbulence is rapidly consumed by the biochemical oxygen demand. The result is anaerobic and reduced conditions as well as a near neutral pH which results in the species of nitrogen found in primary effluent being predominantly the ammonium ion.

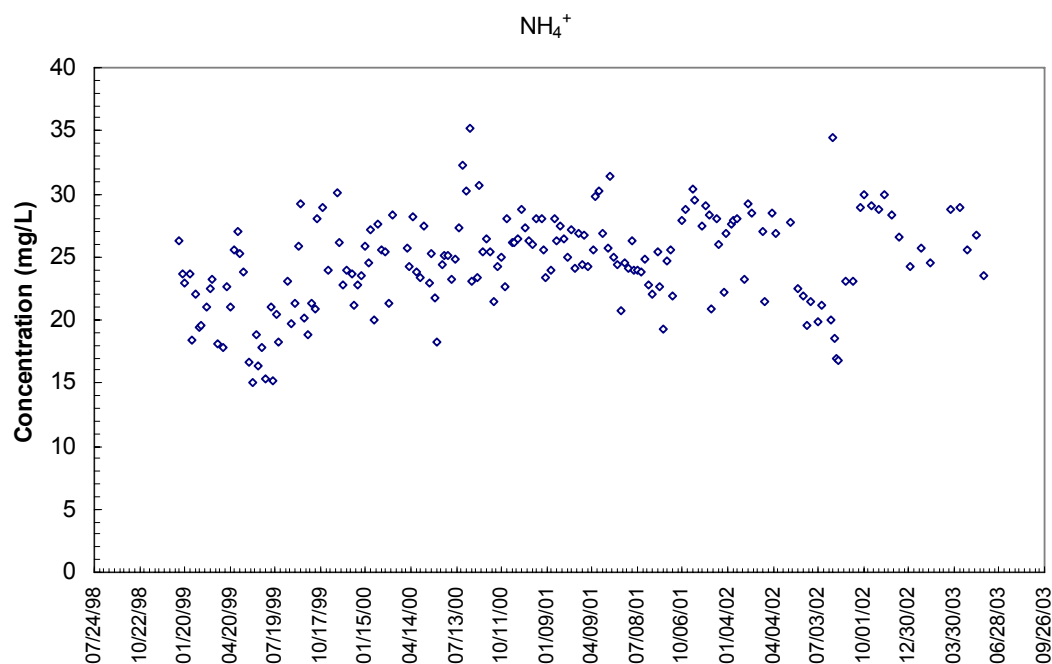
| $\text{NH}_4^+$ |        |        |        |
|-----------------|--------|--------|--------|
|                 | Annual | Summer | Winter |
| Mean            | 24.58  | 23.86  | 25.62  |
| Median          | 24.86  | 24.06  | 26.12  |
| Max             | 35.11  | 35.11  | 30.42  |
| Min             | 15.10  | 15.1   | 18.39  |
| Std Dev.        | 3.70   | 4.06   | 2.82   |
| % Dev.          | 14.9%  | 16.9%  | 10.8%  |

**Table 5: Ammonium ion concentration in Missoula primary effluent.** All values are in mg/L unless otherwise labeled.

Understanding the concentration of ammonia in the primary effluent and in constructed wetlands and the chemistry involved in treating wastewater is important because 1) chemically, ammonia holds the most reduced form of N so oxidation requires more oxygen (approximately 4.3g of oxygen per gram of ammonia oxidized) during it oxidation; 2) due to this reduced oxidation state, ammonia is the preferred form of nitrogen for wetland plant uptake and for autotrophic bacteria, that is, bacteria that make their organic molecules from inorganic raw materials sourced from the environment; and 3) while generally not an issue, the un-ionized form is toxic to a wide range of aquatic life. From the table above one may note slight differences between the summer time concentrations of ammonia and the wintertime concentrations of ammonia. It is unlikely,

due to the temperature and the pH, that ammonia volatilizes off the surface of the primary clarifier as the physical and chemical characteristics of the primary effluent suggest the speciation as the ionized ammonium ion which participates in hydrogen bonding with the water column and therefore is not volatile.

The plot below shows historical  $\text{NH}_4^+$  concentrations in the primary effluent (mg/L) between January of 1999 and May of 2003.

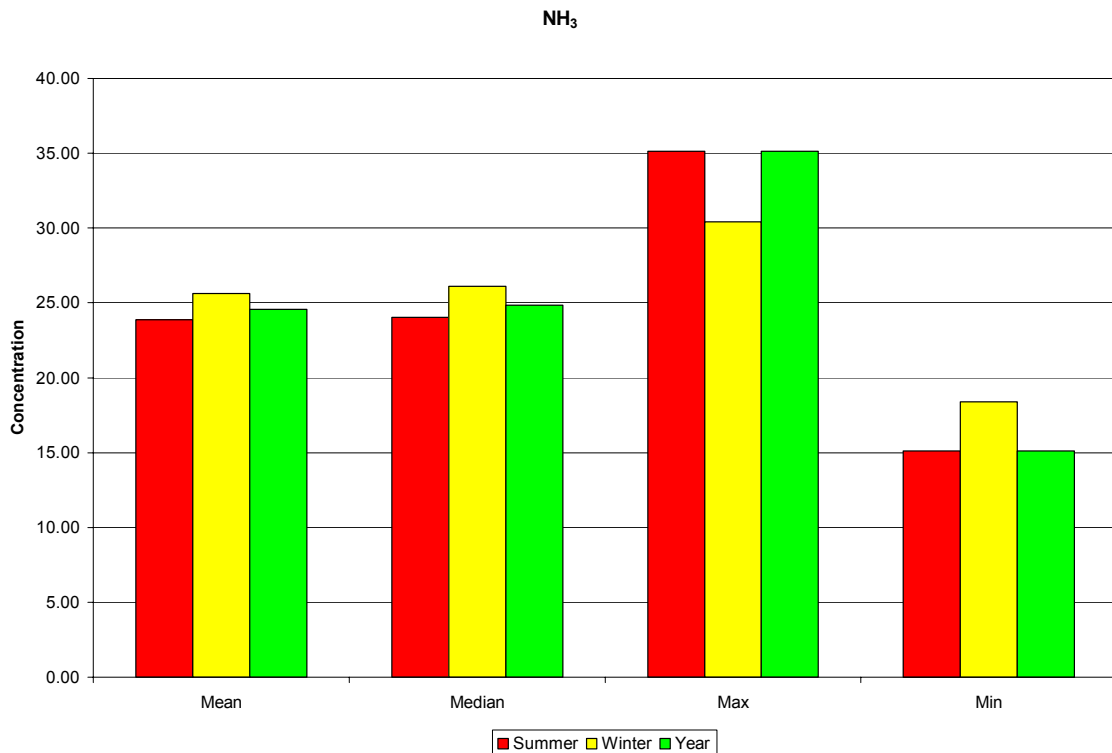


**Figure 10.  $\text{NH}_4^+$  concentration (mg/L) in Missoula primary effluent.** These data, plotted with respect to time, were collected between January of 1999 and May of 2003.

In the plot above variability in ammonium ion concentrations is found between a low of 15 mg/L and high of 35mg/L. Visual inspection of the plot does not suggest any seasonality, however, the two maximum values realized were found during the summer season, but the minimum values did not occur during the winter. The primary effluent

was not aerated nor had any amount of oxygen mechanically introduced so nitrogen remains in a reduced oxidation state.

Another presentation of the data is provided below.

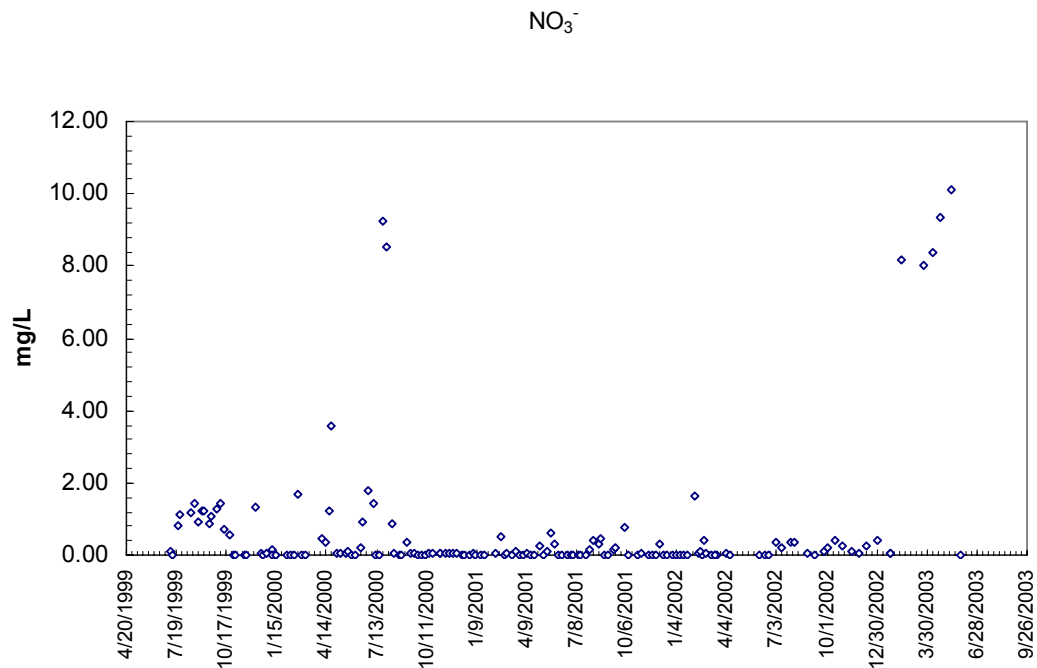


**Figure 11. Average, mean, maximum and minimum of NH<sub>4</sub><sup>+</sup> concentration.** Data were compiled during the summer, winter and annually between January of 1999 and May of 2003.

Overall these data suggest that there is very little difference between the summer time and winter time concentration of NH<sub>4</sub><sup>+</sup>. Ammonia nitrogen is particularly important as it is a critical component that must be treated to meet regulatory compliance. Ammonia is not the limiting design factor for a treatment wetland. However, since ammonia treatment is microbially mediated within a treatment wetland, particular importance must be given to it especially during the wintertime months when microbial activity and plant growth are dormant.

## Nitrate

The next plot shows the nitrate/nitrite concentration. (Nitrite is an intermediate oxidation state of nitrogen between ammonia and nitrate and is generally not stable in the primary effluent or in wetland conditions).

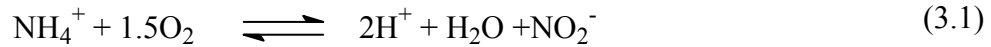


**Figure 12. Nitrate concentration of Missoula primary effluent.** The data are plotted with respect to time between January of 1999 and May of 2003.

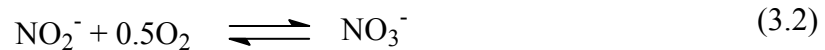
From this plot one may notice again, very little seasonal changes with the concentration of nitrate. Overall, except for periods of operational upset which resulted in spikes in the concentration of nitrate, the concentration of nitrate in the primary effluent is less than 1 mg/L and at times is at fractions of a milligram per liter (mg/L). This is because the reducing conditions found in the primary effluent support an oxidation state of nitrogen at

negative three (-3). The sample times when concentrations in  $\text{NO}_3^-$  spike would suggest that more oxygenated conditions, somewhere upstream of the primary clarifier, resulted in nitrogen moving from a -3 state to the +5 state as found in  $\text{NO}_3^-$ .

It is instructive at this time to review the equilibrium chemistry found between  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . This chemistry is driven by oxygen conditions that are varied throughout the treatment process chemically and biologically. This chemistry is summarized as:



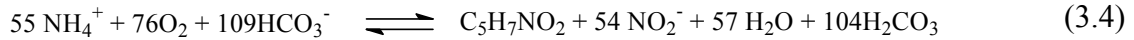
and



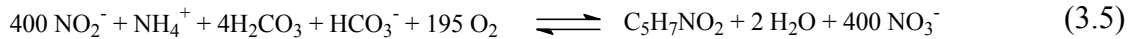
Equation 3.1 is microbially mediated by the bacteria of genus *Nitrosomonas* while equation 3.2, the second step, is mediated by bacteria of the genus *Nitrobacter*. As these equations demonstrate, both steps can only proceed with sufficient amounts of oxygen. In the primary clarifier, very little oxygen is available so the equilibrium shifts to the left. In wetland systems, the oxygen is introduced either by mass transfer from the atmosphere or by respiration via submergent aquatic plants, shifting the above equation to the right. Focusing on the mass transfer oxygen, and understanding that this is a first order process, the nitrification rate in wetlands may also be considered first order (25). The nitrification processes above can be summarized in the next chemical equation.



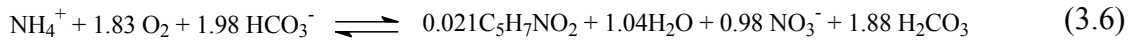
Assessing the stoichiometric relationships in this equation, one calculates that for every one gram of  $\text{NH}_4^+$  consumed in the nitrification process, approximately 3.55 grams  $\text{O}_2$  are required. In addition, for every one gram of  $\text{NH}_4^+$  consumed in the presence of sufficient amounts of oxygen, approximately 0.11 grams of  $\text{H}^+$  are created suggesting that the pH of the wetland systems should reduce as nitrification progresses. The reactions above are microbial mediated and release energy which the bacteria use to create cell mass as  $\text{C}_5\text{H}_7\text{NO}_2$ . The cell synthesis and oxidation reduction reactions are represented below (90):



and

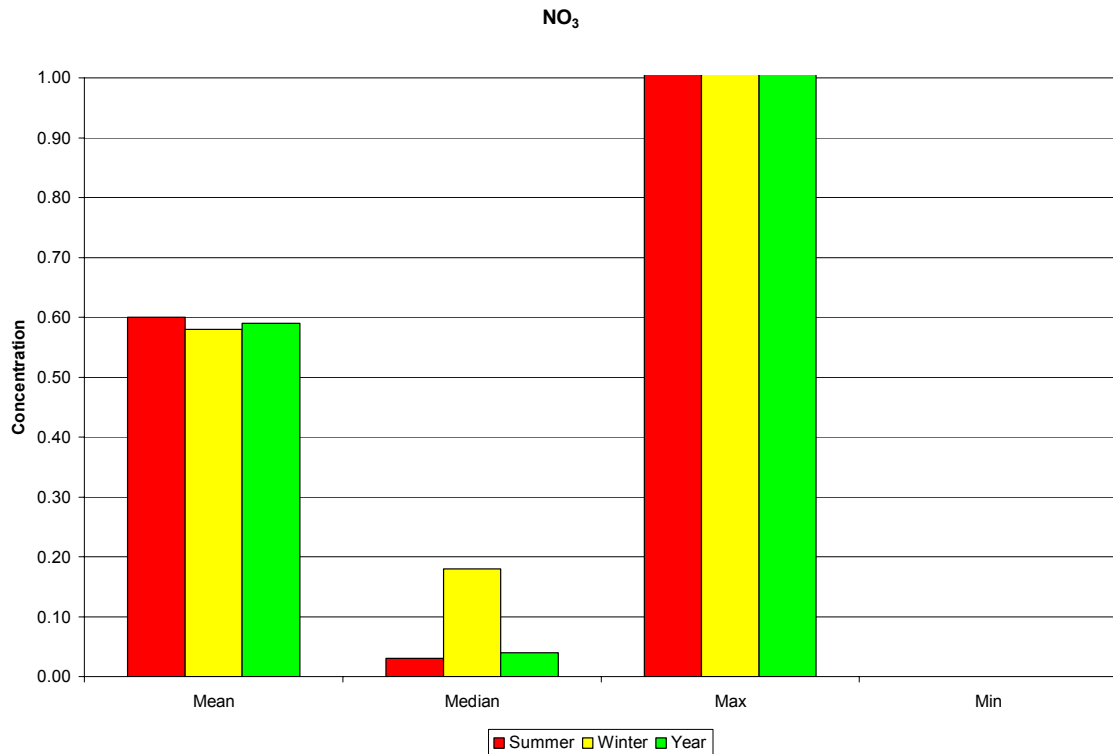


Where equation 3.4 represents the synthesis of nitrosomas cells and equation 3.5 represents the synthesis of nitrobacter. Combining these two equations provides the following:



As demonstrated by the equation above, nitrification consumes oxygen (3.25 g of  $\text{O}_2$  per gram of  $\text{NH}_4^+$ ) and bicarbonate (6.70 g  $\text{HCO}_3^-$  per gram of  $\text{NH}_4^+$ ) in the water and releases water and carbonic acid (6.47 g  $\text{H}_2\text{CO}_3$  per 1 g of  $\text{NH}_4^+$ ) and biomass (131 g per gram of  $\text{NH}_4^+$ ). Also, equations 3.6 and 3.3 correlate closely in terms of oxygen consumption, further validating the microbial mediation of nitrification.

The plot below provides another look at the concentration of nitrate in the primary effluent.

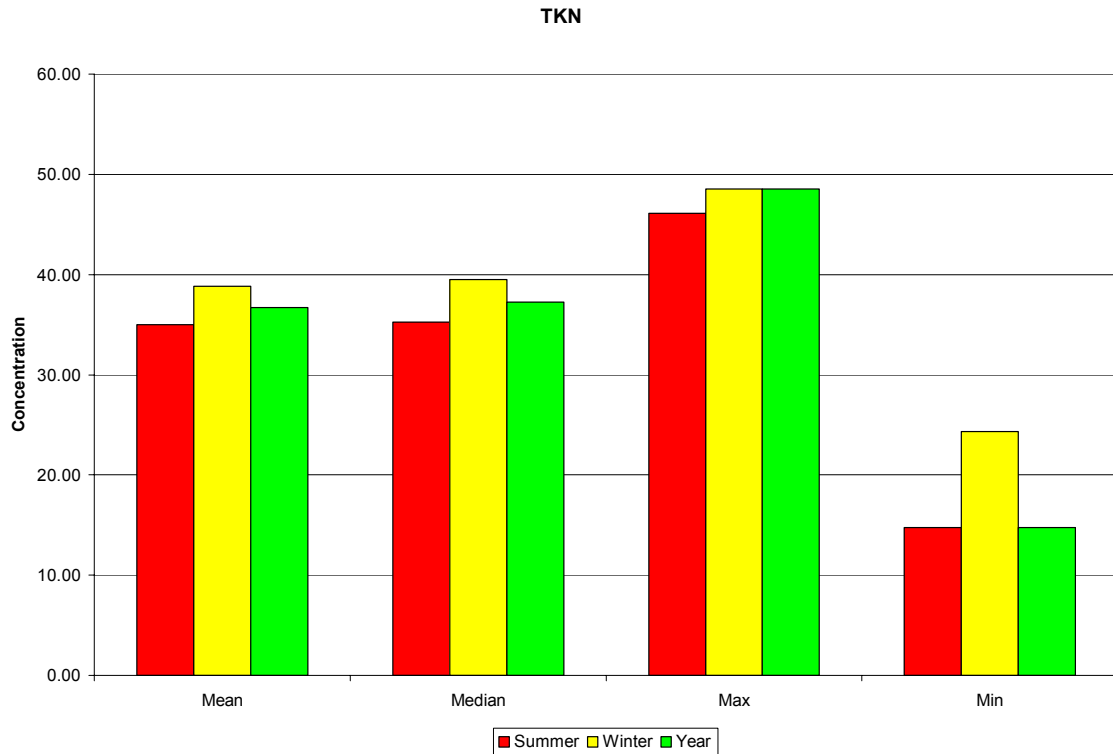


**Figure 13. Mean, maximum and minimum nitrate (NO<sub>3</sub><sup>-</sup>) concentration.** The data represent concentrations found during the summer, winter and annually at the Missoula WWTP. This plot also shows the maximum and minimum values. Values were collected between the years 1999 and 2003.

As this plot graphically depicts, there is very little nitrate found in the primary effluent during either the summer or winter seasons.

## TKN

Below is a plot of the total kjeldahl nitrogen (TKN) concentrations for the primary effluent during the summer, winter and annually from 1999 to 2003. TKN is another critical pollutant whose concentration must be considered during the design of constructed wetland treatment system.



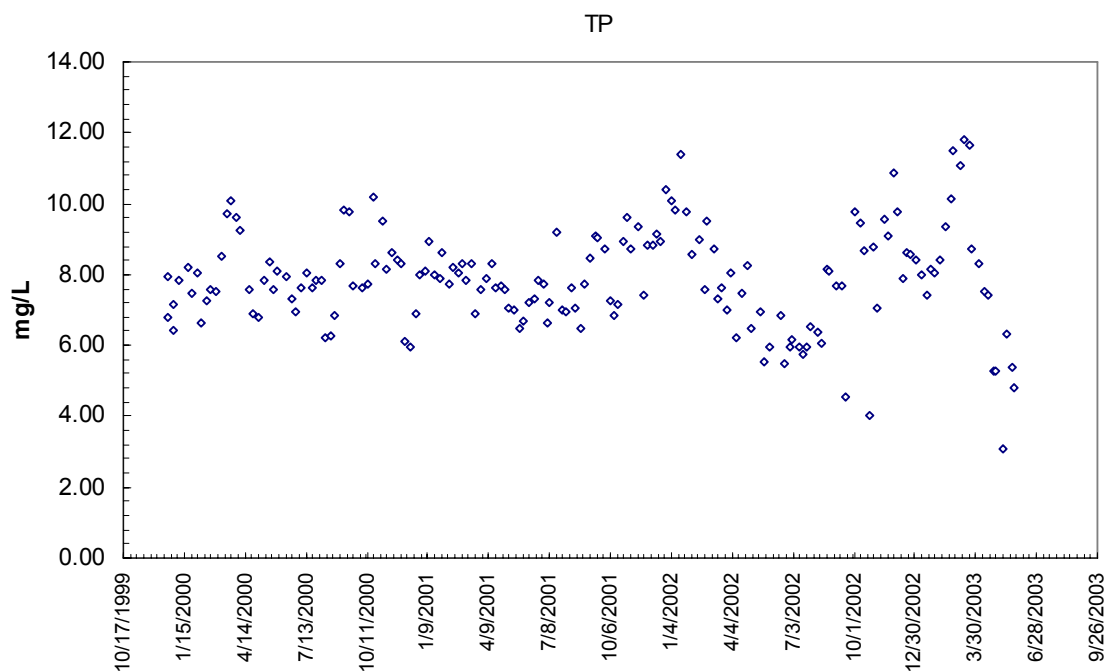
**Figure 14. Mean, median, maximum and minimum TKN concentrations.** Data collected from the primary effluent at the Missoula wastewater treatment plant from 1999 to 2003.

These data presenting in this plot suggests that the mean primary effluent concentration of TKN is slightly higher at 38 mg/L in the winter than in the summer where the concentration is approximately 35 mg/L. Maximum concentration for TKN did not exceed 50 mg/L during the summer or the winter. This is an important consideration for the design of the wetland treatment system as permissible limits are measured as Total Nitrogen (TN). Total nitrogen is determined by adding all species of nitrogen found in the water. Having a predictable and steady TKN concentration entering the constructed wetlands provides for a greater potential of achieving constructed wetland design performance.

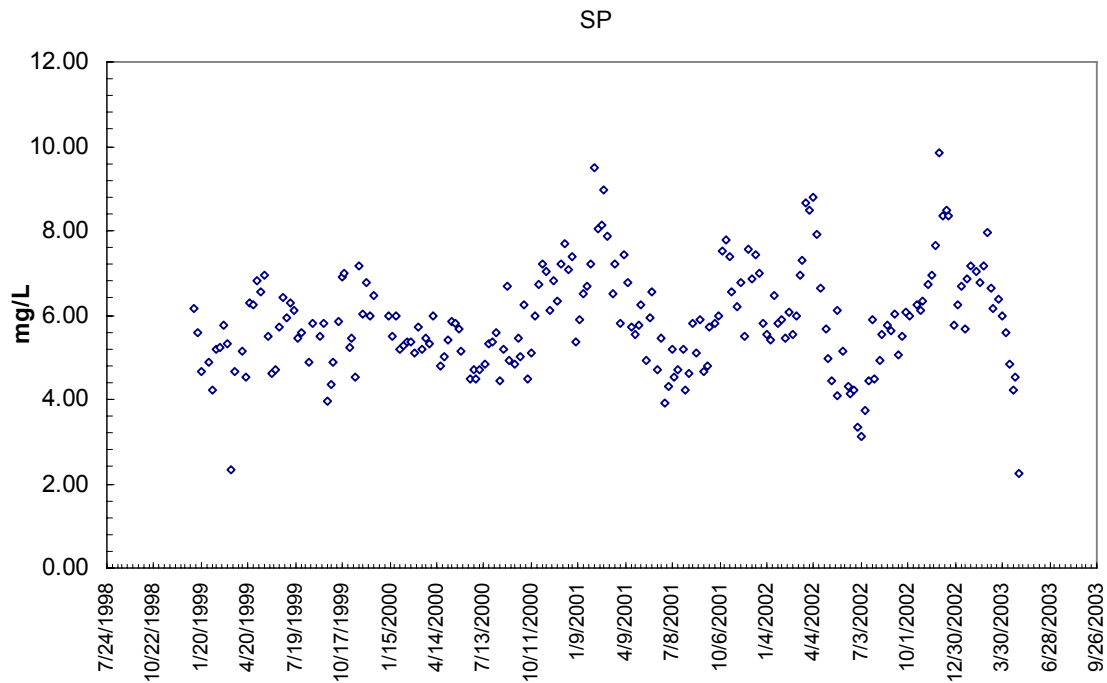
## Phosphorus



An important pollutant to manage at any wastewater treatment plant is phosphorus. Phosphorus (P) is a limiting nutrient for algae growth and elevated levels of P in treatment plant effluent discharged to receiving bodies of water can lead to extensive algae growth and subsequent die-off. The die-off of the algae is particularly important because the microbial degradation of the algae biomass results in the consumption of oxygen. This leads to unnaturally low levels of dissolved oxygen in the water column which can negatively affect aquatic life. This growth and decay process is known as “eutrophication”. In addition, P is the most challenging of the pollutants to treat in both constructed wetlands and in chemically and mechanically intensive large scale treatment systems. Below are plots of total phosphorus (TP) and soluble phosphorus (SP).



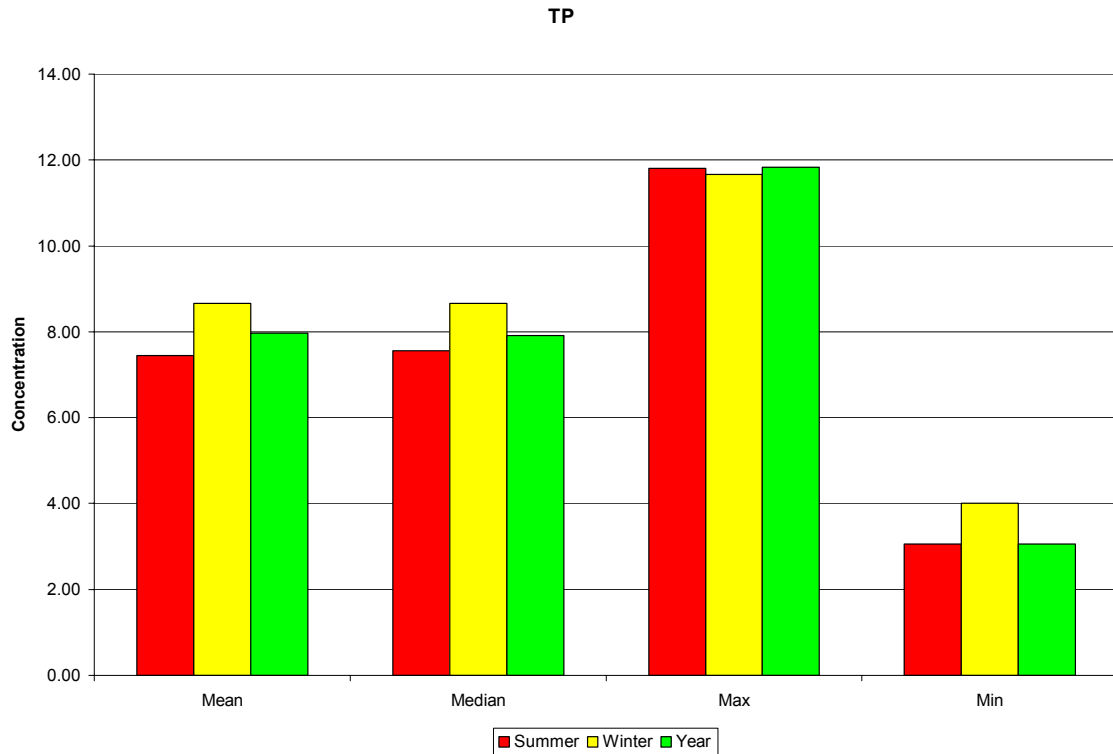
**Figure 15. Total phosphorus in the primary effluent.** These data were collected between January of 1999 and May of 2003.



**Figure 16. Soluble phosphorus in the primary effluent.** The data are plotted with respect to time and were collected between January of 1999 and May of 2003.

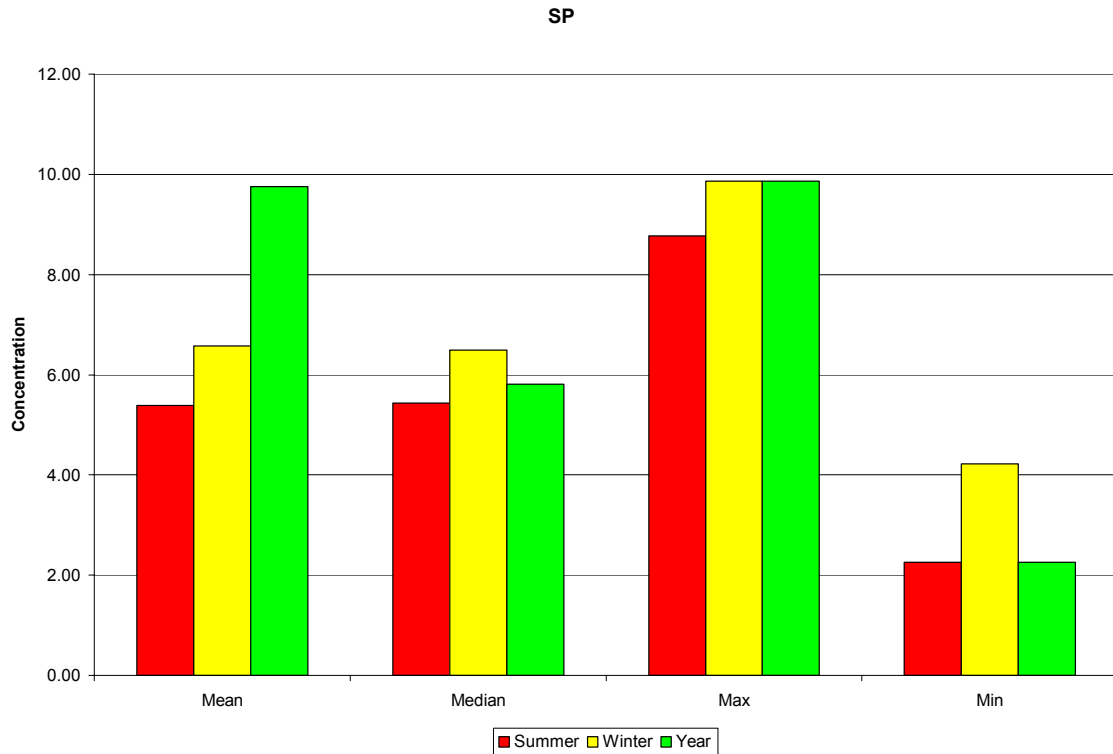
Between the two plots some seasonality is apparent and more so within the analysis of soluble phosphorus. There appears to be a seasonal summer reduction in the concentration of soluble phosphorus in the primary effluent.

Below is a plot of the TP concentrations for the primary effluent found at the Missoula wastewater treatment plant.



**Figure 17. Mean, median, maximum and minimum TP concentration.** Data are for primary effluent from the year 1999 to 2003. Values are in mg/L.

These data suggest, again, there is very little difference between the summertime and wintertime average concentrations of TP. It may be noted, however, that the summertime concentration of TP is slightly less than the average wintertime concentration. Maximum concentrations were slightly below 12 mg/L with minimum concentrations around 4 mg/L. In addition to total phosphorus, soluble phosphorus is important to consider. Soluble phosphorus is that phosphorus that is not bound to any solid substrate suspended in the water and is generally more available as a macronutrient source. Below is a plot of soluble phosphorus concentrations in the primary effluent.

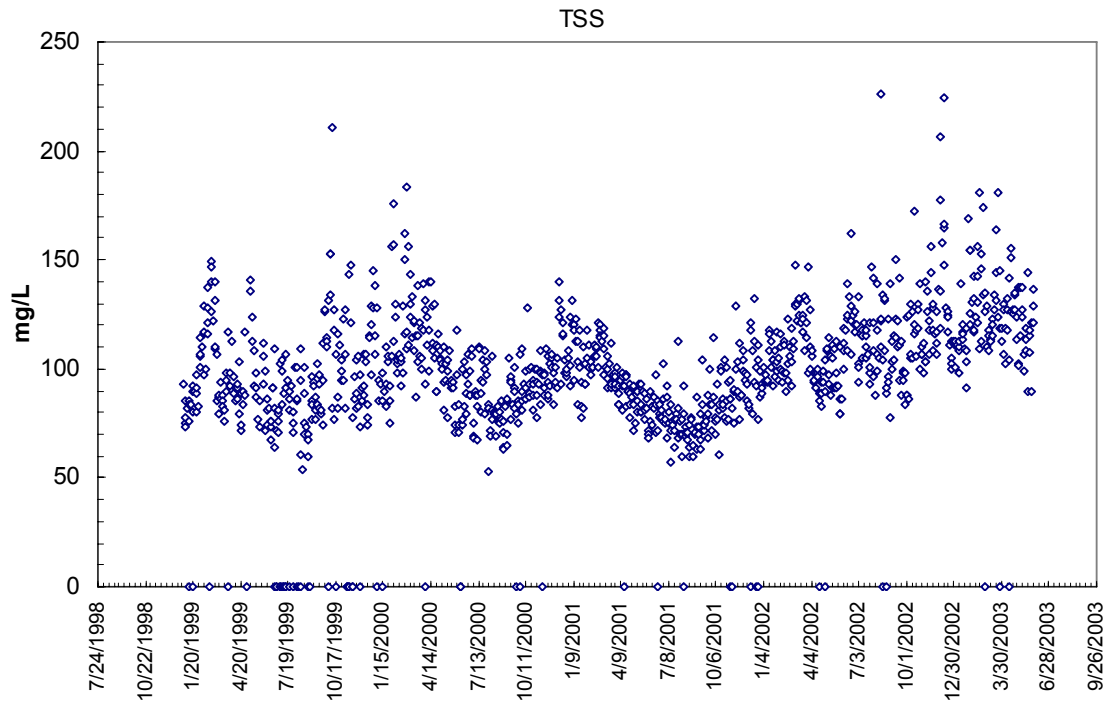


**Figure 18. Mean, median, maximum and minimum SP concentration.** Data were collected from the primary effluent from the year 1999 to 2003. Values are in mg/L.

From this plot, these data suggest that there is a difference between the average SP concentration in the summertime with respect to the SP concentration in the wintertime. The average summer time concentration did not exceed 6 mg/L while the average winter time concentration was slightly below 10 mg/L between 1999 and 2003. As can be noted from the data, the summer time SP is 72% of the TP and the winter time SP is 76% of the TP phosphorus concentration. In essence, SP is the form of phosphorus predominantly found in the primary effluent. This is justified as SP is generally the form in anaerobic conditions found with primary effluent (25).

## TSS

The next plot represents total suspended solids (TSS) data found in the primary effluent.



**Figure 19. TSS in the primary effluent.** These data are presented in mg/L and plotted with respect to time between January of 1999 and May of 2003.

This is an interesting plot in that it demonstrates the challenges presented with wastewater treatment showing both the consistency and variability of primary effluent processed at the Missoula WWTP. In the first and last third of the data there exists no seasonality. However, with the middle portion of the data, there is a strong relationship between the seasons and the concentration of TSS. During this middle third of the data presented, the TSS concentrations are found to decrease in the summer time and increase during the winter. This is thought to be an artifact of the increased population in Missoula during the winter months. It is not understand why there is more variability in the first and last thirds of the data.

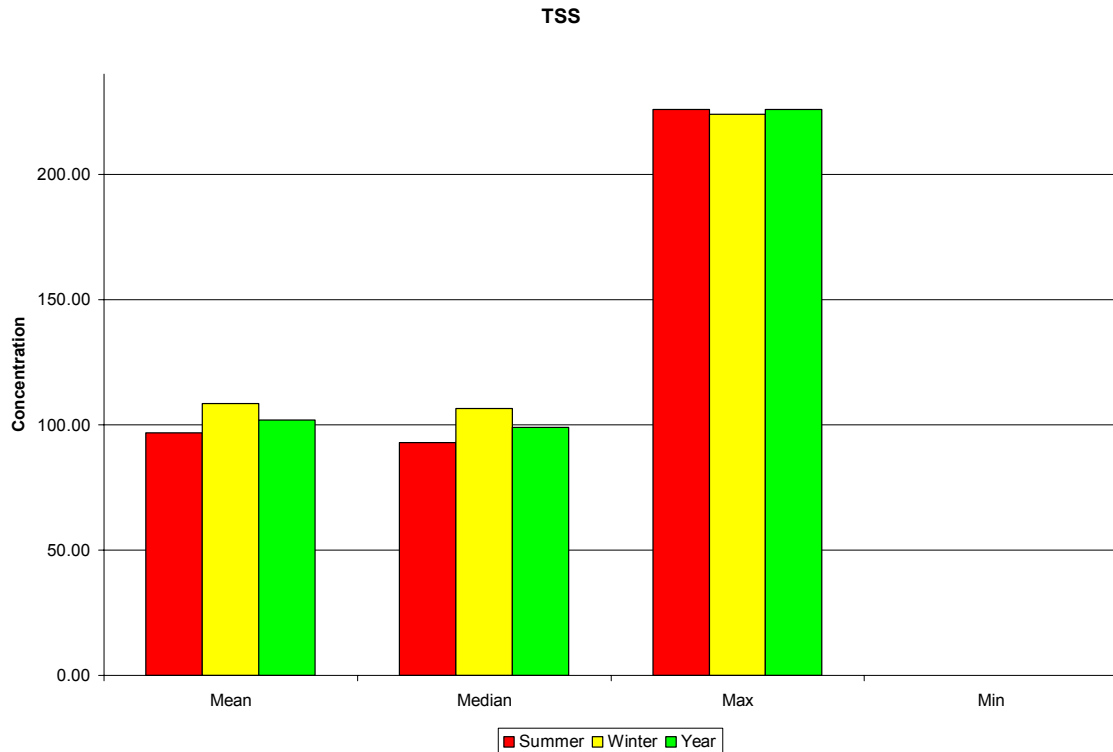
The table below represents the total suspended solid (TSS) concentrations.

| TSS     |        |        |        |
|---------|--------|--------|--------|
|         | Annual | Winter | Summer |
| Mean    | 101.99 | 108.57 | 96.79  |
| Median  | 99.00  | 106.50 | 93.00  |
| Max     | 226.00 | 224.00 | 226.00 |
| Min     | 0.00   | 0.00   | 0.00   |
| Std Dev | 22.62  | 22.33  | 22.25  |
| % Dev   | 22.85  | 20.96% | 23.92% |

**Table 6. TSS summary data for primary effluent.** Data were collected from January 1<sup>st</sup>, 1999 to May 31<sup>st</sup>, 2003. All values are in mg/L unless otherwise labeled.

These data presented in the table suggest, as was the case with BOD, that the TSS concentrations in the summertime are slightly lower than in the wintertime. Although the temperature of the primary effluent is not shared here, it is a factor to consider because as the temperature decreases, the viscosity of water increases. Slight decreases in the temperature of the primary effluent during the wintertime is suspected to reduce the rate at which suspended solids settle thus contributing to a higher concentration in TSS in the primary effluent during the winter months. However, Kadlec and Knight suggest that the physical properties of water that are affected by temperature changes do not significantly contribute to the settling velocity of suspended solids (25). Due to the lack of any natural influences on the mechanical designed primary clarifier, it is therefore concluded that the higher level of TSS found in the primary effluent during the winter time at the Missoula WWTP is directly a result of higher loading rates realized.

Below is a graphical depiction of the TSS data.



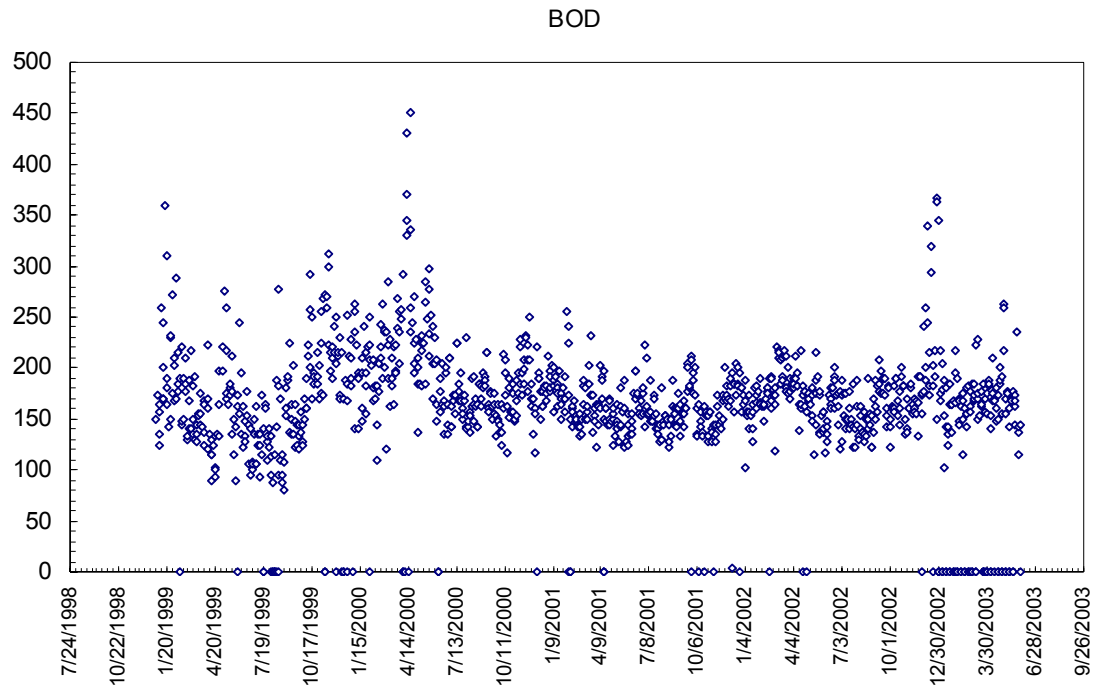
**Figure 20. Mean, median, maximum and minimum TSS concentrations.** Data were collected from the primary effluent from the year 1999 to 2003. Values are in mg/L.

The values for TSS found in the primary effluent hovered around 100 mg/L with the winter time having slightly higher concentrations than the summertime. From this plot and these data there are two anomalies with the maximum values reported as 2138 mg/L in the summer and 940 mg/L in the winter. By taking these data points out of the data set one will find the maximum value of TSS to be 226 mg/L which was found during the summertime. The maximum wintertime concentration of TSS, without considering the anomalies, was found to be 224 mg/L and the average concentration of TSS centered on 100 mg/L.

## BOD

The next pollutant to be considered is biochemical oxygen demand or BOD. Below is a plot showing the concentration of BOD in the primary clarifier between

January of 1999 and May of 2003.



**Figure 21. BOD in the primary effluent.** This is a plot of primary effluent BOD concentration in mg/L with respect to time. Data were collected between January 1999 and May 2003.

These BOD data demonstrate annual consistency with very little indication of strong seasonality and, as expected, there are various times when concentrations spike outside of the normal range of data. These spikes are found during the wintertime which may be related to an operational or mechanical issue.

The eleven hundred and ninety (1190) data points are summarized in the table below.

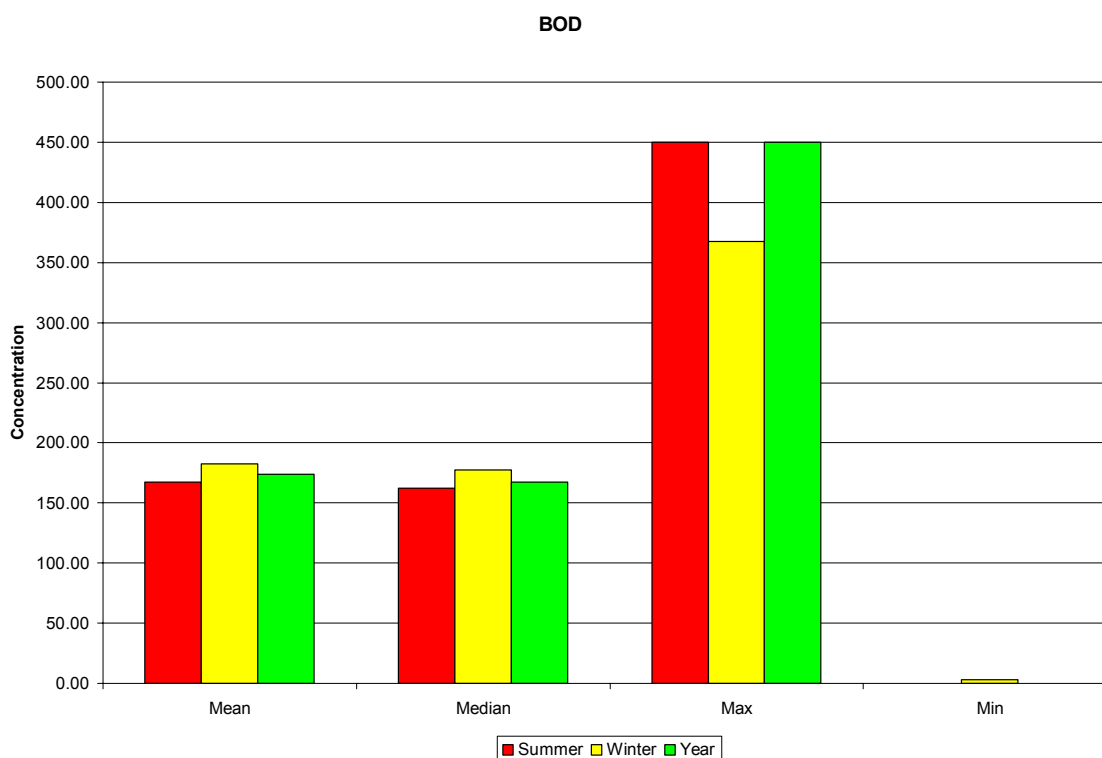


| BOD     |        |        |        |
|---------|--------|--------|--------|
|         | Annual | Winter | Summer |
| Mean    | 173.74 | 182.66 | 167.22 |
| Median  | 167.5  | 177.50 | 162.50 |
| Max     | 450    | 367.5  | 450    |
| Min     | 0      | 3      | 0      |
| Std Dev | 40.64  | 39.71  | 40.10  |
| % Dev   | 24.36% | 22.37% | 24.67% |

**Table 7: BOD summary data for primary effluent.** This table shows a summary of historical concentrations of BOD in the primary effluent at the Missoula Wastewater Treatment Plant. All values are in mg/L unless otherwise specified.

Based on the calendar date, these data points were divided into winter and summer data. From these data for BOD it can be noted that the average concentration of BOD is slightly higher in the wintertime as compared to the summertime. This is suspected to be the result of higher BOD loading rates during the winter time.

Another visual representation of the data is provided below.



**Figure 22. Mean, median, maximum and minimum BOD concentrations.** The data were collected from the primary effluent from the year 1999 to 2003. Values are in mg/L.

From this plot one may note that BOD does not vary considerably between the summertime and wintertime seasons. The value of BOD for the year is just below 150 mg/L. There are some anomalies in the form of maximum spikes in the BOD concentration. However, these are random events that average out over time and therefore need not be considered as a basis of wetland design.

### **Fecal Coliform**

The presence of fecal coliform in water is an indication of the presence of human or animal feces. The fecal coliform is not measured in the primary effluent as in general, the coliform bacteria are too numerous to count.

### **Metals**

Metals in the wastewater are another consideration in the design of a constructed wetland for the City of Missoula. Below is a table showing the metal concentrations of influent wastewater from 1993 and 2002. These samples were taken at the headworks of the treatment facility prior to the primary clarifier.

| Influent | As       | Cd       | Cr       | Cu       | Pb       | Hg       | Mo       | Ni       | Se       | Ag       | Zn       |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Min      | 0.0005   | 0.00005  | 0.002    | 0.005    | 0.002    | 0.00005  | 0.0025   | 0.0025   | 0.0005   | 0.0019   | 0.07     |
| Ave      | 0.002458 | 0.001563 | 0.005333 | 0.069722 | 0.019194 | 0.000256 | 0.005194 | 0.005694 | 0.002236 | 0.011612 | 0.162361 |
| Max      | 0.007    | 0.017    | 0.02     | 0.1      | 0.14     | 0.002    | 0.025    | 0.02     | 0.009    | 0.039    | 1.57     |
| Target   | <0.001   | <0.001   | <0.01    | <0.01    | <0.01    | <0.0001  | <0.005   | <0.005   | <0.001   | <0.01    | N/A      |

**Table 8. Influent wastewater metal concentrations at Missoula.** These data were collected between 1993 and 2002. The bottom line shows the target minimum concentration for the particular metal. All values are mg/L.

As can be seen from the above table, on the average, there are no exceedences of the target metal concentrations in the influent to the wastewater treatment plant. However, note that maximum values all of the metals at some point in time exceeded the target value. Below is a table of the effluent metal concentrations including the target

values. The metals that, on the average, that did not exceed the recommended target on concentration were Cr, Cd, Cu, Pb, Mb, and Ni. Of the metals that did exceed the recommended concentration level, each was not greater than an order of magnitude which suggests that the metal concentration in the influent wastewater is fairly consistent. This is also an indication of the lack of major industry in the Missoula community.

| Effluent |          |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|          | As       | Cd       | Cr       | Cu       | Pb       | Hg       | Mo       | Ni       | Se       | Ag       | Zn       |
| Min      | 0.000250 | 0.000025 | 0.000250 | 0.002500 | 0.000250 | 0.000025 | 0.001250 | 0.001250 | 0.000250 | 0.000125 | 0.002500 |
| Ave      | 0.001182 | 0.000610 | 0.003904 | 0.007045 | 0.005442 | 0.000123 | 0.001811 | 0.002391 | 0.001228 | 0.001475 | 0.054518 |
| Max      | 0.002000 | 0.011000 | 0.030000 | 0.030000 | 0.140000 | 0.000500 | 0.012500 | 0.005000 | 0.005000 | 0.002900 | 0.250000 |
| Target   | <0.001   | <0.001   | <0.01    | <0.01    | <0.01    | <0.0001  | <0.005   | <0.005   | <0.001   | <0.01    | N/A      |

**Table 9. Effluent wastewater metal concentrations at Missoula.** These data were collected between 1993 and 2002. The bottom line shows the target minimum concentration for the particular metal. All values are mg/L.

The balance of the metals is found in the sludge. Below is a table showing the concentration of metals in the sludge from the wastewater treatment plant.

| Sludge |      |      |       |        |       |       |       |       |      |        |         |
|--------|------|------|-------|--------|-------|-------|-------|-------|------|--------|---------|
|        | As   | Cd   | Cr    | Cu     | Pb    | Hg    | Mo    | Ni    | Se   | Ag     | Zn      |
| Min    | 0.15 | 0.5  | 4     | 110    | 7.4   | 0.005 | 1     | 1.65  | 0.44 | 0.25   | 60      |
| Ave    | 4.01 | 3.74 | 51.88 | 668.57 | 90.05 | 4.48  | 12.12 | 15.48 | 5.00 | 120.18 | 1024.78 |
| Max    | 10   | 10   | 310   | 996    | 270   | 16    | 60.5  | 41.5  | 10   | 224    | 8850    |

**Table 10. Sludge metal concentrations at Missoula.** These data were collected between 1993 and 2002. The bottom line shows the target minimum concentration for the particular metal. All values are mg/L.

These values give an indication of what the loading of metals to the wetland substrate may be when using primary effluent. No target metal concentrations are reported in this work. However, application must consider the bioconcentration in animals and metal accumulation in wetland substrate over time.

### 3.3.2 Storm Water Run-off

For the City of Missoula, constructed wetlands can be used to reduce the amount of storm water run-off discharged into the Clark Fork. As rain and snow wash away,

metals and hydrocarbons from the surface of streets and parking lots, the rain water collects in storm drains that discharge to the Clark Fork. The results of which can lead to the accumulation in the watershed of heavy metals and chemicals. By locating constructed wetlands at strategic points of run-off discharge, the water collected may be controlled and treated in the wetland. The unique biological and chemical environment offered by the constructed wetland, based on local conditions and design, may provide a better location for containment and treatment of storm water run-off than direct discharge to the Clark Fork river system.

### ***3.4.0 Constructed Wetlands Cold Weather Performance***

#### **Expectations**

Northern climates and cold weather have proven to have significant impacts on the dynamics within a wetland treatment system. Cold temperatures affect the hydraulics, chemical and biochemical processes, limit plant growth, and slow microbial processes (55). A review of the literature demonstrates that a majority of wetland treatment studies have been conducted with wetland water temperatures warmer than 5°C. However, work has been conducted both domestically and internationally regarding the performance of constructed wetlands in cold weather. Projects in Sweden, Denmark, Austria, and northern USA and Canada demonstrate functionality of constructed wetlands during wintertime operating temperatures (56, 57, 58, 59, 60).

#### **3.4.1 Cold Weather Design**

With this wetland project I will employ a free water surface constructed wetland. Simple stock watering tanks with approximately 500 gallons of total volume are being

utilized. The potential for total freezing of the system is being managed by insulating the wetland perimeter with a combination of road base gravel and straw bales. The road based gravel was back filled around the stock tanks to form a berm with a ~3:1 ratio. The surface of the berm was leveled to accommodate the placement of straw bales. The straw bales extended 6-8 inches above the wetland surface water providing a wind break in an effort to mimic a natural setting.

Distribution manifolds were used for introduction of primary effluent and movement of water from cell to cell. These were located 6 inches below the rim of the stock tanks. This allowed for a 4 inch ice layer to form with a 2 inch margin for continued water flow. This ice layer did form during the coldest months of the year of operation and flow was able to be maintained throughout the wetland. Water temperature within the wetland under the ice layer varied from 0.5°C to 3°C with the higher temperature noted during periods of primary water addition. Because of the heat contained in the primary effluent, the ice layer thickness was reduced during additions of primary effluent. The primary effluent averaged 12°C during the coldest months of the year. During additions, the ice layer in cell #1 (the first cell receiving primary effluent) nearly melted. However, it re-formed at the later stages of the treatment cycle. The maximum ice thickness was 4 inches which coincided with what is experienced at the Ronan, MT surface flow treatment wetland (61).

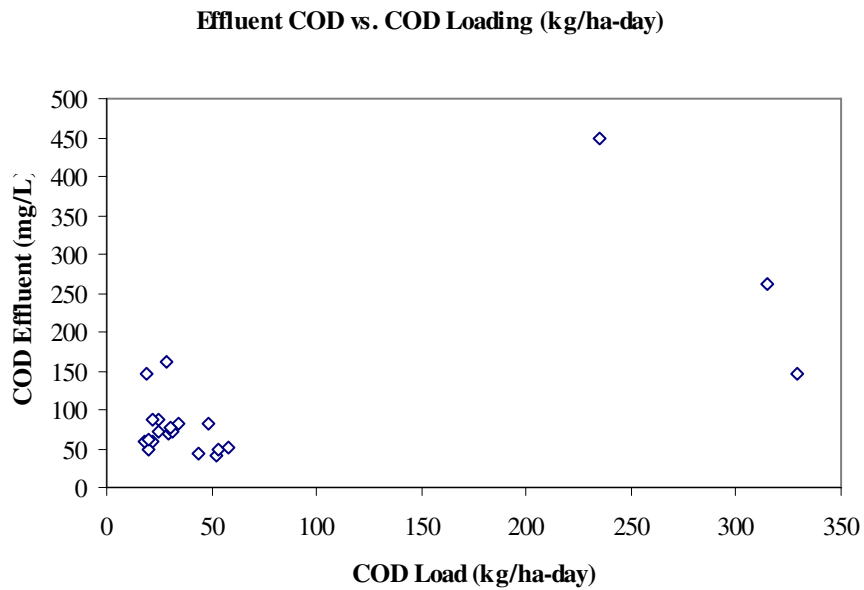
### ***3.5.0 Loading Considerations and Treatment Performance***

#### **3.5.1 BOD/COD**

Treatment performance can be measured as the relationship between average areal loading rate and average effluent concentration. Free water surface wetlands should not

be designed for an areal loading of greater than 60 kg/ha-day of BOD. Maintaining a loading rate less than this maximum has resulted in consistent effluent attainment of <30mg/L of BOD (51). The weekly average permit limit for BOD is 40 mg/L and the monthly average BOD permit limit is 25mg/L (63).

Chemical oxygen demand (COD) loading rates were measured for 21 additions of primary effluent to the experimental constructed wetland over the course of the first year. The average seven day loading rate was 69 kg COD/ha-day. This produced an average COD effluent concentration of 105 mg/L. Utilizing a power relationship between COD and BOD of  $y = .001(x)^{2.0828}$ , the calculation suggests an average BOD effluent concentration of 16.2 (where  $x = [\text{COD}]$ ). This means that loading of approximately 69 kg COD/ha-day would generate an average BOD effluent concentration of less than 20mg/L. Below is a chart showing loading rates of COD and COD effluent concentration generated by the experimental scale constructed wetlands.



**Figure 23. COD effluent concentration based on load rate.** The plot is of COD effluent vs. COD load for 21 additions of primary effluent to the WWTP constructed wetland.

This plot suggests that higher COD loading rates can potentially be achieved.

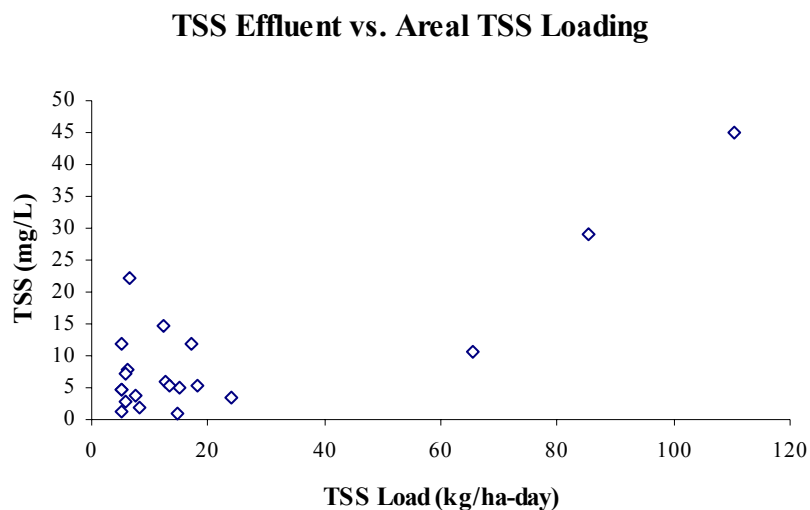
Only one data point, however, supports this suggestion as a correlation with low effluent COD concentrations. With this data point I have a COD loading rate of 329 kg/ha-day and a COD effluent of 147 mg/L which equates to a BOD effluent concentration of 32 mg/L. More additions need to be made in the COD loading range of 100-250 kg/ha-day to quantify the long-term potential effluent concentrations.

### 3.5.2 Total Suspended Solids (TSS)

Constructed wetlands have been determined as an effective way to treat TSS (25). TSS removal occurs predominantly near the inlet of the constructed wetland (64). In pilot studies at the Arcata treatment wetland, 80% of TSS was removed in the first two days of the theoretical hydraulic retention time (51). It is suggested that a maximum

areal TSS loading rate not exceed 50 kg/ha-day to attain consistent effluent concentrations less than 30 mg TSS/L.

TSS loading rates were measured for 21 additions of primary effluent to the Missoula pilot wetland during the first year of data collection. The average TSS loading rate was 21.4 kg/ha-day and the average effluent concentration was 9.77 mg TSS/L. These numbers were well below the recommended loading concentrations from the EPA suggesting that a higher loading of TSS is possible. Below is a chart representing the TSS effluent concentration plotted against the TSS loading rate. This plot suggests that there is consistent performance in TSS removal at areal loading rates up to 25 kg/ha-day and one data point suggests that a loading rate of 65 kg/ha-day will achieve TSS effluent concentrations below 15 mg/L. This data point was generated in June 2002 suggesting that spring time operating conditions allow for increased loading rates of TSS.



**Figure 24. TSS effluent concentrations based on the load rate.**



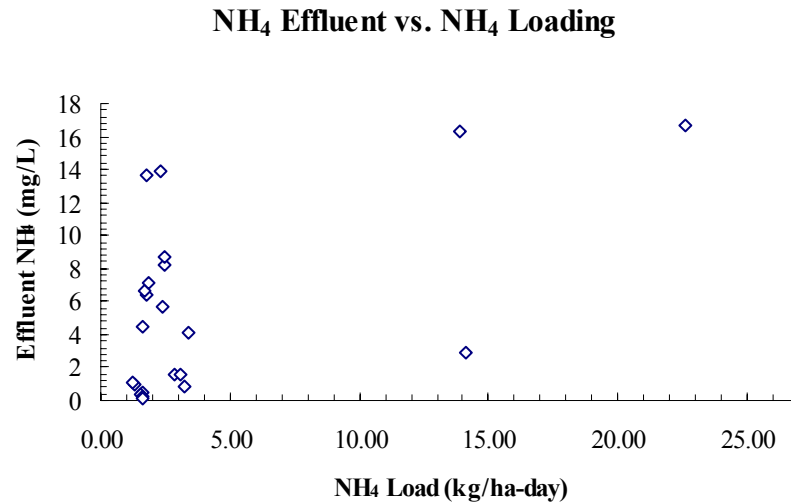
Additional data on springtime loading rates of TSS need to be conducted to confirm this performance assumption as the figure suggests that higher loading rates place the effluent TSS concentration above permit limits.

### 3.5.3 Nitrogen

Target total nitrogen discharge concentration through the Voluntary Nutrient Reduction Plan (VNRP) is 10mg/L. Design of the wetland treatment system must take into account the chemical processes that convert organic and inorganic nitrogen to nitrate through nitrification and subsequently nitrify nitrate for removal of TN from the system. Maximum TN loadings should not exceed 5 kg/ha-day to achieve a TN concentrations of less than 10 mg/L. It is necessary to design constructed wetland systems with ample open water zones for conversion of TKN to  $\text{NO}_3$  and ample vegetated zones (anaerobic/anoxic) for denitrification (51). Denitrification is contingent upon a source of carbon which is sufficiently provided by decaying biomass within the wetland. It is reported that 100 mg of  $\text{NO}_3\text{-N/L}$  is capable of being degraded by carbon produced from decay of macrophytes (64).

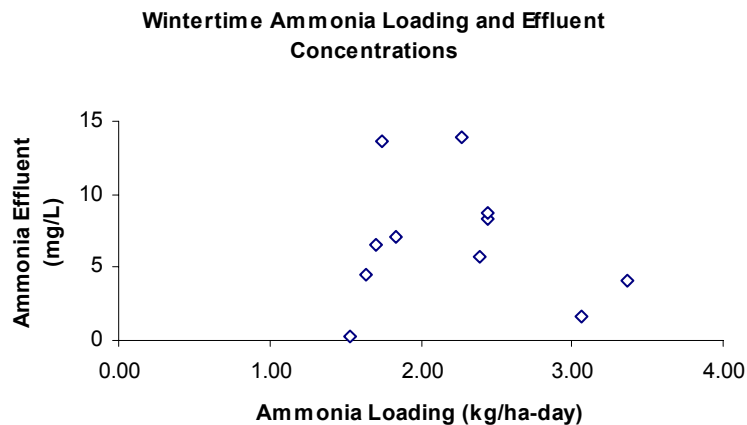
During the first season of study, the treatment of  $\text{NH}_4^+$  in the experimental wetland system was investigated. These initial data suggested an average  $\text{NH}_4^+$  loading rate of 4.3 kg/ha-day produced an average  $\text{NH}_4^+$  effluent concentration of 5.8 mg/L.  $\text{NH}_4^+$  removal is attributed to nitrification with the data indicating an average ammonia effluent concentration of 6.8 mg/L from October 15, 2002 to March 15, of 2003 (wintertime). This suggests that other  $\text{NH}_4^+$  removal mechanisms are taking place. These initial data demonstrated an annual average reduction of ammonia in the experimental wetland of 70.43%. The average reduction of ammonia during the winter

months was 63.9%. Below is a chart showing ammonia effluent concentrations with respect to areal ammonia loading rates.



**Figure 25. Ammonia effluent concentrations based on load rate.**

These data presented in this plot suggest that there is no direct correlation between ammonia loading and ammonia effluent concentrations.



**Figure 26. Ammonia effluent concentrations based on winter loadings.** Data were collected from mid-October of 2002 to mid-March 2003.

Again, under wintertime conditions, there is no distinct correlation between the effluent ammonia and the loading rates. However, at all loading amounts the effluent concentration was less than the current permit discharge limit of 15 mg NH<sub>4</sub>/L. At higher loading rates of approximately 3 and 3.5 kg/ha-day, the ammonia effluent was less than 5 mg/L. These two data points were generated on 10/15/02 and 10/22/02 during the first month of wintertime performance studies. During these loadings the wetland experienced a 56% and 95% reduction in water temperature, respectively. The remaining wintertime data experienced an average 76% reduction in wetland water temperature.

Additional work needs to be conducted based on TKN loading rates. Published TKN loading rates and corresponding treatment performance suggest a TKN loading rate not greater than 5 kg/ha-day to achieve a TKN effluent of 10 mg/L. Given that the majority of nitrogen from the primary clarifier is NH<sub>4</sub><sup>+</sup> a loading rate based on ammonia of 5 kg/ha-day suggests an achievable effluent concentration less than 10 mg/L with sufficient open water zones.

### **3.5.5 Phosphorus**

Constructed wetlands, if properly designed, may be capable of removing phosphorus from wastewaters both in the short-term and in the long term. However, on a per unit area basis, wetlands are not efficient phosphorus removers (25). The area required for phosphorus removal is the largest of all the wetland requirements and generally exceeds the land areas realistically available adjacent to most wastewater treatment plants. Phosphorus removal by harvesting biomass has to date not proven feasible (25). In addition, increases in biomass should not be counted as long term, sustainable, or permanent removal of phosphorus. Phosphorus removal mechanisms are

by precipitation and adsorption with calcium, aluminum, and iron generally in the substrate of a subsurface flow system (65). Media selection with subsurface flow wetlands can play a role in sustainable removal of phosphorus. Brix *et al.* report that sands with a high concentration of calcium in combination with crushed marble mixed in with the bed media of a subsurface flow constructed wetland can enhance the phosphorus adsorption capacity (65). Other media have demonstrated phosphorus removal capacity. These include light-weight expanded clay aggregates (LECA), granulated laterite, shale, and crushed marble (66, 67, 68, 69).

Phosphorus analysis conducted at the Missoula-WWTP showed no reduction in soluble phosphorus (SP) over the course of a seven day treatment. No subsurface treatment mechanisms were employed.

### **3.5.6 Fecal Coliform and Pathogens**

Fecal Coliform removal is a result of flocculation and sedimentation (70). Additional fecal coliform removal is from irradiation by ultraviolet sunlight which is the main mechanism for fecal coliform removal found in lagoons (71). Fecal coliform contribution from wildlife was studied in treatment systems that receive chlorinated effluent. Gearheart *et al.* reports that the mean fecal coliform in the effluent was 40 CFU/100mL, was less than 300 CFU/100mL 90% of the time and on no occasion exceeded 500 CFU/100mL (72).

### **3.5.7 Mosquitoes and Vector Control**

Constructed wetlands, especially surface flow wetlands, are attractive to all types of wildlife. This may be regarded as a benefit however there are detractors such as

mosquito habitat development which may prove an obstacle to permitting, funding and or the site of the wetland (51).

Several methods have been used to manage mosquito populations. Predation via mosquito fish (*Gambusia*) is one means of biological control (73). The gambusia, a non-native predator fish introduced from the southeastern U.S., are resistant to the fluctuating water quality found on a constructed wetland treating municipal wastewater. Optimum vegetation, however, must be managed to ensure successful gambusia breeding and a sustained population. Generally gambusia cannot over winter however a group out of Nebraska has bred a cold tolerant variety that may over winter (74). *Gambusia*, in some locations, is regulated as a non-native predator species they may eat and harm young native fish, frogs, and salamanders, and beneficial aquatic insects (76). Keeping this in mind, use of the non-winter tolerant fish variety may eliminate the problem of competition with native species and reduce potential for non-native species introduction and proliferation.

The natural food web is also an excellent manager of pest species. Amphibians such as frogs and salamanders and dragonfly larvae and also many aquatic insects feed on mosquitoes. Birds such as swallows and bats consume mosquitoes as well (75). Vegetation also plays a role in mosquito population control. Tall vegetation that falls over in winter and accumulates reduces the opportunity to use biological or chemical control agents (77).

Chemical control agents have significant environmental impacts and should be considered very carefully prior to use. Larvicides such as *Bacillus thuringiensis israelensis* (B.t.i.) can be introduced into the water column for effective control of

mosquito larvae and offer an alternative to adult population control via chemical agents. In addition, B.t.i. is considered less of an environmental impact than application or spraying of adult mosquito chemical control agents (75).

Other options include mechanical control through the use of aeration pumps to disrupt the surface of the water, but this introduces more maintenance and management costs and is inconsistent with the concept of a passive treatment system.

### **3.6.0 Wetland Structures (*Plants, Substrate, Liner*)**

#### **3.6.1 Plant Selection and Resources**

Natural wetland systems provide a diverse selection of wetland plant species to choose from for constructed systems. Each plant may overlap with treatment functions. Effective constructed wetland design and operation requires a basic understanding of growth requirements and characteristics of native wetland plants (25). In general, the more plant diversity a wetland treatment system maintains, the healthier and more robust the system tends to be. With a healthy and robust system better performance characteristics may be achieved. In general a treatment wetland will need subsurface plants (submergent plants that grow below the surface of the water), emergent plants (plants that grow above the surface of the water), and floating aquatic (plants that reside on the surface of the water). Each of these plants provide for various functions.

The submergent plants provide oxygen to the water column. As sunlight penetrates the surface of the wetland, the plants inhale  $\text{CO}_2$  and respire  $\text{O}_2$ . The basic design function for submergent plants therefore is oxygenation of the water column. As demonstrated by the chemistry of nitrification, approximately 3.55 g of  $\text{O}_2$  is required for every gram of  $\text{NH}_4^+$  consumed in nitrification.

Floating plant species have buoyant leaves and stems that allow for floating on the water surface (25). Floating plant species, such as duckweed, provide a biological mat on the surface of the water that limits both sunlight penetration and oxygen diffusion into the water column. This serves the functions of controlling algae populations, and keeping the conditions of the wetland anaerobic or reduced (77). In addition, this biological mat limits and controls the mosquito population by providing a non favorable environment on the water surface that limits mosquito larvae production and creates habitat for larvae predation. However, floating aquatic plants can become a nuisance and invasive to a constructed wetland whose water surface was designed to be open and free of plants. In situations such as these, management practices may need to be developed such as the daily removal of duckweed to ensure open water zones are truly open to the atmosphere. Also, wind action on the surface of a wetland can push and move these biological duckweed mats, which may alter desired chemical characteristics of the water column by allowing sunlight to penetrate and oxygen to diffuse.

Emergent plant species (e.g. cattails and bulrush) are the third type of wetland plant that may be utilized in a constructed wetland treatment system. These plants are perennial and generally are rooted in the substrate of the wetland and propagate rhizomally through their root system. Essentially, tubers send out shoots that result in new plant growth. These shoots or stalks of the plant provide a surface upon which a microbial film may develop and where treatment action may take place and these surfaces are generally where the chemical assimilation processes occur as one of the treatment mechanisms (25). This microbial film on the surface of emergent plants is

similar to fixed film bioreactors that are used as a mechanism to treat municipal waste water.

Woody plant species with extensive root systems can penetrate and potentially compromise clay liners and structural berms. Perimeter management of these types of plant species is important.

### **3.6.2 Substrate Selection and Resources**

With the two wetland treatment options, surface flow and sub-surface flow, there is a corresponding need for two different types of substrate. For the experimental constructed wetland using a surface flow design, the planting media consisted of 4:1 ratio of Eko-Compost to coarse road base gravel. Materials available on site or near-by were utilized and were sufficient for a planting medium for a free water surface wetland. The medium was prepared to a depth of 4, 6, and 8 inches (78). It is recommended that the rooting medium be a minimum of 8 inches and sufficiently compacted. This enables the root structure of the plants to have a secure hold in the soil. Lack of sufficient medium depth may result in the plants being uprooted and suspended in the water column. This uprooting was experienced at the constructed wetland at Missoula and was caused by persistent windy conditions. If plants are uprooted and subsequently pushed by wind forces across the water surface, the operational design parameters may be changed and maintenance costs can potentially incur.

A limited discussion on subsurface flow (SSF) wetland media is provided here. The medium for the subsurface flow (SSF) wetland generally consists of various types of gravel, sand, and crushed stone. In some cases (as in Germany), there are systems that are still in use where the medium is soil. It is recommended that for a SSF system the



medium vary with depth. For example, the bottom layer should consist of the large river rock, the next layer should decrease in diameter to course gravel and the upper layers should be a fine gravel or course sand. Each of these media provides sufficient hydraulic conductivity. Of important note is that the hydraulic conductivity will decrease over the lifetime of the SSF and excess hydraulic conductivity must be designed into the system.

### **3.6.3 Liner**

In general, the permeability of the underlying soil and the policy of the state permitting agency decide when and what type of liner is required (25). Constructed wetlands for municipal wastewater treatment in Montana must be lined (78). In the Missoula Valley the soils have high permeability. Infiltration of untreated wastewater into the aquifer from a constructed wetland is a concern in a poorly designed and managed system. Liners may consist of a clay lens, bentonite soil layers, chemical treatment of existing soil, asphalt, and synthetic liners such as polyvinylchloride (PVC) or high density polyethylene (HDPE). When a clay liner is utilized, the thickness is approximately 6 inches. However, larger liner thickness combined with a thicker substrate depth may be needed to prevent the liner from being compromised by plant root systems. Clay liners have advantages in that they can be placed in any shape chosen by the wetland designer, however they can be compromised by woody plant roots. Synthetic liners are less sustainable and limit the variability in cell shape, however, are very easy to install and have demonstrated performance.

### ***3.7.0 Cost of Construction, Operation and Maintenance***

#### **3.7.1 Construction Cost Overview**

Due to the land requirements associated with natural treatment wetlands the construction costs are determined on a per acre basis (1 hectare is 2.4711 acres). Average cost for surface flow constructed wetlands is estimated at \$26,557 per acre with an average operating cost of \$582 per cubic meter per day ( $\$/\text{m}^3/\text{d}$ ) of treatment (79, 80). The major costs with surface flow wetlands are with earthwork (25, 81). The subsurface flow (SSF) wetlands cost about eight times more than surface flow wetlands. The average cost for subsurface flow wetlands is \$218,752 per acre (25). The larger cost associated with subsurface flow wetlands are attributed to the gravel fill which represents as much as 50% of the capital cost (25).

#### **3.7.2 Maintenance and Operation Costs**

High biological activity within the experimental wetland system and use of straw bales as the insulation for the system resulted in the restriction of water flow between each wetland cell. Periodic maintenance on the experimental treatment wetland included cleaning of the catch basin pump and cleaning of the distribution manifolds located at both the inlet and outlet of each wetland cell. A routine maintenance procedure would have to be developed and implemented to maintain water flow and design performance of a larger scale treatment wetland.

### ***3.8.0 Land Requirements and Wetland Costs***

An analysis was conducted to determine the total land requirements and wetland cost to treat wastewater at the City of Missoula. The goal was to target 10,500,000

gallons of water treatment per day (40,000 m<sup>3</sup>/day) with a total nitrogen effluent concentration (C<sub>MM</sub>) of approximately 10 mg/L. The total nitrogen loading rate (A<sub>R</sub>) was fixed at 5 kg TN/ha-day. Using this information, the area of the wetland (A<sub>w</sub>) necessary can be determined using the following equation:

$$A_w = [(Q_{AA})(C_{MM})*(1\text{kg}/1\times 10^6 \text{ mg})*(1000\text{L}/1\text{m}^3)]/A_R \quad (3.1)$$

The calculations are presented in the table below.

| Gal/day (MM) | Q <sub>AA</sub> m <sup>3</sup> /d | Q <sub>MM</sub> m <sup>3</sup> /d | C <sub>MM</sub> mg/l | A <sub>R</sub> kg TN/ha/d | B <sub>p</sub> | A <sub>w</sub> (ha) | A <sub>w</sub> (ac) | A <sub>T</sub> (ha) | A <sub>T</sub> (ac) | D <sub>w</sub> (m) |
|--------------|-----------------------------------|-----------------------------------|----------------------|---------------------------|----------------|---------------------|---------------------|---------------------|---------------------|--------------------|
| 14,529,460   | 37,850                            | 55,000                            | 10                   | 5                         | 1.3            | 76                  | 187                 | 98                  | 243                 | 1                  |
| 10,566,880   | 30,000                            | 40,000                            | 10                   | 5                         | 1.3            | 60                  | 148                 | 78                  | 193                 | 1                  |

**Table 11. Constructed wetland design calculations for Missoula.**

Included in this calculation was a 30% buffer zone (B<sub>p</sub>). Total land requirements to treat 10.5 million gallons per day (MMGD) of effluent and to achieve an annual average TN effluent concentration of 10 mg/L would require a free water surface wetland area of 148 acres (600,000 m<sup>2</sup>) with a total area with a total project area of 192 acres including the 30% land buffer. From the equation below, the hydraulic retention time can be determined using the annual average daily waste water flow rate (Q<sub>AA</sub>) of 30,000 m<sup>3</sup>/day and a depth (D<sub>w</sub>) of 1 m.

$$\text{HRT} = (V_{\max})(e)/Q_{AA} \quad (3.2)$$

The symbol e represents the volume of the wetland made up by plant material and is given a value of 0.875 meaning 87.5 percent of the wetland volume is actually water with the balance being plant structure. This equation yielded an estimated 17.5 days of hydraulic retention time which is 7.5 days higher than the suggested minimum hydraulic retention time of 10 days. This accounts for the growth of plant material as the wetland matures (e as discussed above), which may reduce the overall volume of the wetland and

hence, reduce the retention time. Total costs excluding land price is estimated at \$5.18 million dollars (~\$27,000 per acre).

In conversations with the City of Missoula, I estimated that the City will have approximately 5 acres of total land area after the BNR expansion. The City is interested in using a wetland system as a “natural buffer” that could provide additional treatment capacity to the treatment plant and provide other aesthetic benefits. Using equations 3.1 and 3.2, and with a 30% land buffer the potential wetland area could be 3.85 acres. If loaded at 5 kg N/ha-day with a target effluent concentration of 10 mg/L, the wetland can treat approximately 266,000 gallons of wastewater water per day with an average retention time of 15 days. Total cost for this treatment wetland is estimated at \$135,000 excluding potential additional land costs.

### ***3.9.0 Design Recommendations and Conclusions***

This preceding information and the preliminary work conducted thus far suggest that total treatment of all of the Missoula wastewater produced with constructed wetlands not feasible. This is due in part to the land constraints, cost constraints, and performance variability found in wetland treatment systems. The results of this study did however suggest that partial treatment of a portion of the final or primary effluent in a smaller scale wetland treatment system is possible and is worthy of additional investigation. This would consist of a natural system integrated into the current mechanical treatment process. This integrated treatment system may provide a natural buffer for treatment capacity whereby the wastewater treatment operations could use the natural system during times of process disruption where discharge to the Clark Fork River is exceeding

permissible limits. In addition, the wetland effluent could be re-used in some revenue generating fashion that is yet to be determined.

There are a number of options for the City of Missoula treatment plant from what has been discovered over the course of this feasibility analysis. It is the author's conclusion that no single natural treatment system alone will provide the necessary treatment required to sustain permitted discharge limits. If the City of Missoula determines that a natural treatment system is the direction it wishes to take, it is recommended that a combination of alternative treatment options be investigated and employed to reduce the nutrient impact on the Clark Fork River. This combination should include a free water surface, an integrated system of hybrid poplars, and potential irrigation or land application.

In summary, constructed wetlands are not viable options for total treatment of all the wastewater generated by the City of Missoula. However, on a smaller scale, constructed wetlands may provide services to the treatment plant in terms of 1) periodic additional capacity, 2) aesthetic and educational outreach, 3) a local source of information and demonstration through which surrounding rural communities in the Clark Fork Watershed may understand the practical merits of wetland treatment systems for their particular community.

## **4.0.0 Objectives of This Work**

The objective of this work is to build a small scale experimental wetland treatment system and evaluate the seasonal treatment performance against regulatory discharge permit limits. Included in this is demonstration that kinetics associated with the treatment of various pollutants may not be valid. The evaluation of actual chemical kinetics found in this experimental wetland system differed from kinetics presented in the literature. Additional work is centered on understanding the potential for the seasonal re-use of wetland effluent water in the irrigation of industrial oilseed crops for renewable fuel production. From this evaluation a simple predictive model has been developed which communities may utilize for the rapid evaluation of constructed wetlands as a potential option for the treatment of municipal wastewater coupled with the re-use of effluent water for generation of a sustainable source of transportation fuel for use in the public works. Based on the results of the City of Missoula feasibility study as presented in section 3.0.0, the application of this work is targeted for smaller rural communities with wastewater flows of less than 1 million gallons per day and having access to large tracts of tillage adjacent to the site location.

### ***4.1.0 Experimental System Design and Development***

Considerable thought and planning was put into the experimental system design. A variety of experimental systems were reviewed with the goal of using local materials within the budget constraints of the project. A visit to Humboldt State University and the laboratory of Dr. Robert Gearheart provided a base model upon which the Missoula experimental constructed wetland was designed. Specifically, the design was derived

from a smaller scale system that was utilized at Humbolt State University in Arcata, California for various undergraduate and graduate thesis investigations in the environmental engineering department.

The system for the Missoula investigation focused on a free water surface design with multiple cells with each cell, in theory, providing a different treatment function. A free water surface (FWS) constructed wetland is one where the water surface is open to the atmosphere as compared to a subsurface flow (SSF) wetland where the wetland water flows below the substrate level.

An experimental constructed wetland system was installed outside and adjacent to a primary clarifier at the City of Missoula wastewater treatment plant (WWTP) in Missoula, Montana, USA. The system utilized four locally available 1900-L live-stock watering tanks (Figure 1). These tanks were plumbed in series using three-quarter inch (3/4 inch) diameter, schedule 40 polyvinylchloride (PVC) piping and three quarter inch (3/4 inch) diameter valves and other various and readily available PVC and high density polyethylene (HDPE) plumbing and fittings. The system consisted of these four stock tanks, termed “cells”, each with targeted design functions. The wetland had a surface area that was calculated to be approximately  $21 \text{ m}^2$  and a depth of approximately 0.65 m giving a total volume of approximately  $13.7 \text{ m}^3$ . This volume accounted for the void volume (e) of approximately 12.5 % attributed to plant growth. The hydraulic retention time for the experimental wetland system was approximately 9.5 days with a designed flow rate of  $1.23 \text{ m}^3/\text{day}$  (325 gallons/day).



**Figure 1. Photo of experimental constructed wetland system in Missoula.** The system was installed at the Missoula Wastewater Treatment Plant, Spring 2002. Cell 1 is in the background with Cell 4 in the foreground. The wastewater treatment plant's primary clarifier safety railing is visible at the left edge of the photograph. Note the open water zone of Cell 2.

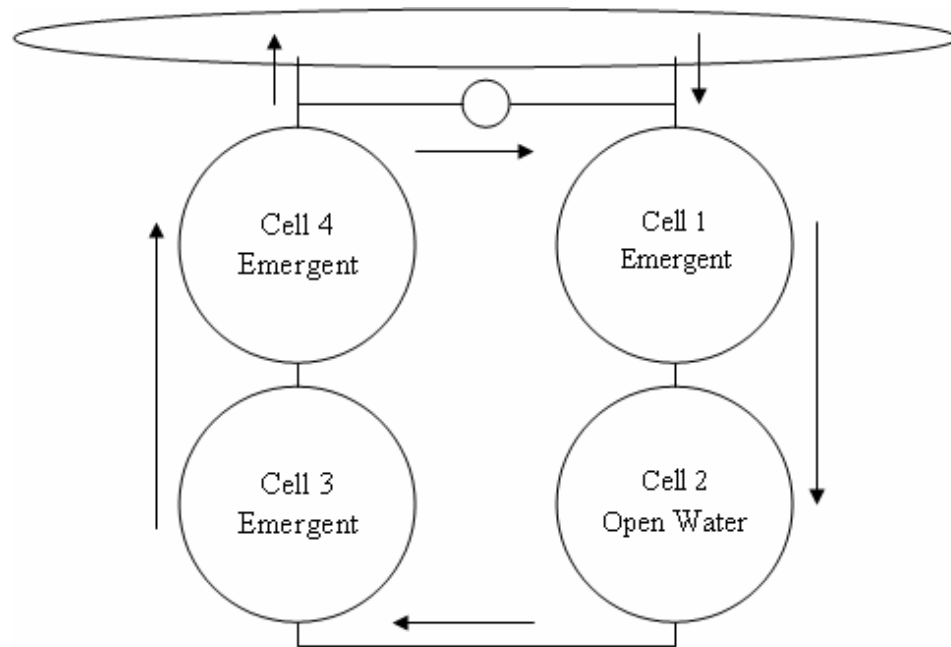
Cell 1 (in the background of figure 1) received the initial inflow of primary effluent. The primary effluent was pumped into Cell 1 via a submersible pump placed in the launderer of the primary clarifier. The intended design function of Cell 1 was to reduce the flow rate of incoming clarifier effluent and facilitate the treatment of biochemical oxygen demand (BOD) and total suspended solids (TSS). To accomplish this, the cell was planted with emergent bulrush vegetation (*Scirpus tabernaemontani*) and floating duckweed vegetation (*Lemna spp*). {Author Note: Additional discussion regarding wetland plants is found in Section 5.0.0 Wetland Macrophytes} The *Scirpus*, (the tall emergent plants in Figure 1 above) in addition to providing a surface for



microbial growth slowed and distributed the influent water being pumped into the system. The *Lemna* (the green colored material floating on the surface of Cell 1 in the photo above) generated a surface cover that limited atmospheric oxygen diffusion.

Cell 2, the second cell in the system, was designed to be an open water zone. Open water zones have no vegetated surface covering or emergent macrophytes (see Figure 2 below). Cell 2 employed submergent vegetation as common pondweed (*Potamogeton vaginatus*) with the intent of adding oxygen to the water column through photosynthesis (25). With BOD being treated in cell 1, the respired oxygen found in cell 2, in theory, provides an electron source for the oxidation of ammonia nitrogen to nitrite followed by nitrate.

Below is a schematic diagram for the flow through the system showing the cell numbers as well as the return loop to recycle treatment water.



**Figure 28. Simple flow diagram of the experimental wetland system.** The large elliptical image is the primary clarifier with the smallest circle representing the recycle basin as the return loop.

Cell 3 and Cell 4 employed both emergent bulrush vegetation and floating duckweed. The intended design function was for the duckweed to provide a surface covering to limit oxygen diffusion and promote denitrification. In addition, these two cells provided a polishing of the discharge water, removing BOD and TSS that may have been generated in the system from additional biomass production (*e.g.*, algae).

Several devices were used for managing hydraulic flow through the experimental system each of which is discussed here. Each cell utilized distribution manifolds at both the inlet and outlet. The manifolds consisted of  $\frac{1}{2}$  inch PVC tubing with a series of  $\frac{3}{8}$  inch holes drilled in the PVC tubing. The manifolds, presumably, provided even

dispersion as the wastewater traveled through each wetland cell. Cell 4, the last cell, and cell 1, the initial cell, were connected via a recirculation basin. This allowed primary effluent to be added to the system with the ability to continuously re-circulate the treatment water. A vacuum-activated level switch submerged in the catch basin engaged a small electrical pump which pumped wetland effluent from cell 4 back to cell 1. The back pressure created by elevating the water into cell 1 was managed by a check valve. This check valve prevented back flow from Cell 1 to the recycle catch basin. The water level in each cell was maintained approximately 6 inches above each distribution manifold.



**Figure 29. Photo of Cell 2 prior to water and plant introduction.** The substrate is Eko-Compost. Note the distribution manifolds for the even distribution of water through the cell.

Each cell contained locally available materials as the planting medium. The substrate utilized consisted of road-base gravel blended with organic compost material from EKO Compost, Inc., whose operations are adjacent to the Missoula WWTP. As explained in section 3.6.2, the substrate for the system was prepared by blending 4 parts

compost to 1 part road base gravel material. The blended substrate was evenly distributed in each cell at an average depth of 20 cm.

A detailed discussion of wetland plants is provided below in section 5.0.0. All vegetation used in the treatment cells was obtained locally from natural wetland features. The Missoula WWTP is located on the banks of the Clark Fork River. Downstream from the WWTP, a series of backwater sloughs retain water throughout the year. These sloughs support a diverse community of wetland plants. Of particular interest was *Scirpus tabernaemontani*. *Scirpus* tuber masses were transplanted during the summer season of 2001 from this natural wetland feature and placed in Cells 1, 3 and 4. The cells were partially flooded to just submerge the tubers until it was evident that new shoots were coming from the tubers. Within a matter of days new *Scirpus* shoots were evident and the water level was gradually increased in parallel with their growth. *Lemna* was introduced to the wetland in Cell 4. The rapid growth of *Lemna* in Cell 4 provided sufficient transplant resources for the other cells.

The pilot scale system did not involve or require any subgrade excavation. In an effort to mimic subgrade conditions, an insulation berm was established around the system. The berm consisted of the same road base gravel utilized as part of the substrate and straw bales purchased from Mountain West Cooperative on North Reserve Street in Missoula. Road base was backfilled around the cells two-thirds the height of each cell with an average thickness of 18 inches (~45 cm) and leveled out on top. Straw bales were placed on top of the level berm surface around each cell. Voids that formed between the rectangular straw bales and the circular cell were backfilled with road base material. This combined road base and straw bale backfill insulation satisfactorily

mimicked subgrade conditions and in practice prevented complete freeze up of the system, which allowed for experimentation throughout the winter months.



**Figure 30. Photo of the experimental system during the winter.** Exposed plumbing was wrapped with a heating wire and insulation. This prevented the freezing of pipes and valves under the wintertime operating conditions.

Water flowed passively through the system by head pressure created from the loading of the primary effluent to cell 1 and mechanically by head pressure generated by subsequent effluent pumped through the recycle catch basin.

Construction of a new biological nutrient removal system (BNR) at the Missoula WWTP required the system to be moved during the three year experiment. Over the course of one week the system was drained, partially dismantled and moved to a new location. The new location required the system to be reconfigured slightly so as to maximize the available space.

#### **4.2.0 Generate Local Data**

As discussed above, an objective of this project was to generate a local, in-state understanding of the seasonal performance of constructed wetlands treating municipal waste water. Important data to collect are the loading rates of each pollutant that a wetland system can handle on a seasonal basis. These loading rates help with the overall design of a system for a particular community based on the pollutant profile and wastewater flow rate. The loading rates combined with effluent concentration data can assist other rural communities in determining the acreage that may be irrigated for biomass or oilseed crop production.

For a wetland treatment system that may discharge to a receiving body of water, the treatment performance must be sufficient to meet regulatory discharge permit requirements. These permit requirements are determined by the Montana Department of Environmental Quality (MT DEQ) through total maximum daily loads (TMDLs). Permit holders are required to submit discharge data on a regular basis. The state reviews this data to determine compliance (or lack of) with the discharge permit regulations given the watershed's particular TMDL. Prior to constructing a wetland for treatment of municipal wastewater and discharge for treatment with effluent re-use, it is critical that the municipality contemplating the use of these types of systems understand the anticipated treatment performance for their specific wastewater characteristics and application. As such, small experimental scale systems may be a beneficial and a low cost way to understand the feasibility of using a full scale constructed wetland to treat municipal wastewater.

Furthermore, a particular area of interest in this work is the actual seasonal treatment characteristics and the chemical kinetics associated with the seasons. The individual seasonal treatment performance (autumn, winter, spring and summer) and the seasonal kinetics have not been investigated thoroughly in constructed wetland treatment systems. Blanket assumptions, on an annual basis, have been made for constructed wetland treatment performance. It is suspected that each season presents its own unique benefits and challenges for the treatment of wastewater in constructed wetland systems. Therefore, it is important to understand each season and the treatment characteristics of each season in the overall design of a system.





## **5.0.0 Wetland Plants – Macrophytes**

The discussion of wetland plants in this dissertation will be limited to a qualitative overview of vascular varieties. That is, varieties with cells joined in tubes that transport water or in general have tissues that are easily visible with the naked eye (82). In addition, our discussion is centered on obligate wetland plant varieties, those varieties that are exclusively found in wetland habitats as apposed to facultative varieties that are found in both wetland and dry land ecosystems (25). Understanding the needs of wetland plants and what wetland plants inhabit specific geographical areas is essential to long term wetland treatment system performance in terms of the design specifications.

Wetland plants can be classified as floating, submergent and emergent. Floating plants generally do not have rooted structures and are found on the surface of the water with buoyancy maintained by broad leaves. These varieties are found generally in deeper areas (depth >0.50 m) of a wetland ecosystem. Submergent species are found in the same deeper water areas as floating varieties, however, these plants are rooted with buoyancy maintained by both stems and leaves. Submergent and floating species cannot tolerate a total loss of water and must, at all times, have some standing water within which to grow. Emergent species have plant structures open to the air above the surface of the water. Certain emergent species, unlike floating and submergent varieties, can tolerate periods when no standing water is present in the wetland.

Wetlands also have monocot and dicot plant varieties. Monocots have one cotyledon or seed leaf in the embryo while dicots have two cotyledons in the embryo. Leaf veins are generally parallel for monocots and netlike for dicots. Vascular structure for monocots is complex while dicots have systematic ring formations. Monocots utilize

a fibrous root system while dicots employ a taproot. The taproot found in dicots is an important consideration when considering management of the liner material and substrate planting material and depth. Flowering parts of monocots are in multiples of three while dicots have multiples of four or five (82). The discussion and utilization in this particular study revolves around monocot varieties.

Natural wetlands support a wide range of plant species and this is a desired feature in constructed wetlands. Plant diversity is primarily due to a moisture rich environment found in both natural and constructed wetland systems. Moisture, a limiting factor for plants in non-wetland environments, however, does not mean that all plants thrive equally. Within wetland systems there exists the traditional ecological competition among plant species. Because the diversity of plant species in wetland treatment systems is one of the attractions of their application in wastewater treatment, it is critical that wetland diversity be initiated from the beginning and maintained and managed throughout the useful life of the system.

Wetland plant diversity is very important in a treatment system. Easily recognizable, cattail (*Typha spp.*) is a fast growing hardy wetland plant variety that is considered, at times, a nuisance species as it can dominate a wetland ecosystem and limit diversity. This plant is generally associated with all wetland type environments and if not introduced during construction of the system, may eventually volunteer and become part of or the dominate the emergent plants within the wetland treatment system.

### **5.1.0 Plant Selection**

Selection of plant varieties for any wetland treatment system is important. The varieties used in the constructed treatment system should reflect the varieties that are

indigenous to natural wetland systems in the region. Introduction of non-native or hybridized species to a constructed wetland system is not especially favorable and may cause unnecessary, unexpected and persistent problems. The designer of the constructed wetland treatment system may look at the local to regional natural wetlands for an indication of the plant varieties that may thrive and be appropriate in a constructed system designed for treatment of municipal wastewater. Overall, recent work suggests that vascular plants are not the dominant factor in nutrient treatment and that their nutrient uptake is a small fraction of the overall treatment performance (83). With this understanding and published data to support this assumption, the selection of wetland plants indigenous to the region is the most logical and cost effective approach to establishing a healthy and diverse plant community.

Three of the dominate pollutants considered for treatment in wetland treatment systems are BOD, TSS and fecal coliform. Recent work conducted on small scale systems treating household wastewater suggest that polyculture systems, systems with numerous and diverse varieties of plants, provide the best and most consistent overall treatment performance of these household wastewater pollutants throughout the year (84). Additional work suggests that the bacterial community is strongly influenced by the type of wetland system employed (sub-surface flow or free water surface), the substrate (gravel, sand, soil, or mixtures) and the plant varieties utilized (85). Therefore, selection of suitable plant varieties should be based on the goal of having diversity with additional consideration of a 20-year operating period and the dynamic growth cycle of certain varieties and species. Twenty years is a reasonable public planning time frame and engineering assumption of the operational life of a constructed wetland treatment

system. Within these twenty years the changes in the wetland plant community may vary dramatically and must be accounted for in the overall performance assumptions keeping in mind the tremendous amount of nutrients available to the plant systems as compared to a natural wetland feature. In addition, the selection needs to include plants with the potential for large a surface area as the physical structure of the plant, in particular the submerged physical structures, provide a surface for microbial film development. While not investigated in this work and an important consideration in terms of available surface area provided by plant species, publications have suggested that the biofilm that develops on the surface of submerged plant structures (*i.e.* leaves and stems) is the primary location of chemical transformation and treatment of pollutants (86, 87)

In this experimental wetland treatment system the plant varieties were chosen because of their presence in local nearby natural wetlands. The emergent species chosen was *Scirpus tabermontani* commonly known as bulrush. Floating species of *Lemna minor* or lesser duckweed volunteered during the transplant of the bulrush and were also introduced. A single submergent plant was introduced of the genus *Potamogeton* however the species was not identified. This submergent plant is commonly known as pondweed and has short oval shape leaves. Based on this, I assumed that the plant was *Potamegeton amplifolius* or commonly known as large-leaf pondweed.

### **5.2.0 Plant Source, medium and method of introduction**

The plants for the constructed wetland treatment project were acquired locally. Adjacent to the City of Missoula wastewater treatment plant is the Clark Fork River. The Clark Fork with head waters near Butte, MT progresses through the Missoula Valley on its way to the Columbia River in Washington. In the Missoula Valley sloughs have been

created that are connected to the river during spring run-off and in some cases are fed via ground water upwelling. The sloughs support a variety of wetland plants. A particularly large slough is located just downstream from the wastewater treatment plant. This slough provides ideal habitat for bulrush, duckweed and large leaf pondweed.

Limited understanding on the methods for successful transplanting of wetland plants was maintained by the author. Some basic assumptions were made in that wetland plants need water and if a rooting species, a substrate within which to anchor. Knowing that the water supply would be sufficient, attention focused on the rooting medium or substrate in the wetland. As discussed above, the rooting medium consisted of 4 parts EKO-compost<sup>®</sup> with one part road base gravel. The medium, as discussed before, was evenly spread to a depth of approximately 20 cm on the floor of each stock tank.

The method of transplanting was very basic and employed simply a shovel and a dozen five gallon buckets. A tuber mass of bulrush was dug utilizing a shovel. Each tuber mass had between 3-6 standing “stalks” of bulrush. (Bulrushes grow rhizomally so it was necessary to sever each tuber mass along the main rhizome root structure. When doing this, concern was taken not to severely disrupt or over harvest the natural system so that recovery is guaranteed.) Each tuber mass was placed in a five-gallon bucket and transported to the experimental wetland site. Once at the wetland site, each tuber mass was placed in wetland planting substrate in the stock tank. After transplant, the stock tank was gradually filled with water.

Lemna were transplanted within five-gallon buckets using a small amount of standing water upon which the plants floated. Submergent plants were transplanted in a similar fashion to the bulrush.

### **5.3.0 Conclusions**

Plants contribute an important role within a constructed wetland system. Diversity in employing native varieties with a large surface area is vital. In addition, emergent, submergent, and floating species should be utilized. It is recommended that plant species be selected and introduced so as to prevent a mono-culture or a single dominant plant species or variety. For example, in order to prevent a mono culture of cattails this work introduced bulrush (*Scripus tabermontani*) as the first wetland plant. It is suggested that bulrush varieties be the initial plant introduced into larger constructed wetland treatment systems. This allows the bulrush to establish a presence in the wetland structure prior to introduction or volunteering of cattails. Overall, the wetland plant species need to be selected based on a 20-year life cycle of the operating system.

## **6.0.0 Sampling and Analytical Methods**

The methods used for the analysis of wetland samples followed procedures utilized by the Missoula wastewater treatment plant laboratory for their discharge permit reporting requirements. These are methods approved by the US EPA in the analysis of wastewater and were derived from Standard Methods (91) and from Lachat Instrumentation, Inc. of Milwaukee, WI.

### ***6.1.0 Biochemical and Chemical Oxygen Demand***

#### **Introduction:**

Biochemical oxygen demand (BOD) is the most frequently used method to determine and measure the carbon content within a given aquatic system (25). In a wetland treatment system, carbon is both introduced to the wetland and generated within the wetland. Production within the wetland is a result of numerous wetland decomposition processes and was not investigated in this project. In general, the carbon cycle within a wetland is tremendously complex and this process is simplified by focusing on the measurement and treatment of BOD (25).

Carbon is reduced in the wetland systems through the uptake of  $\text{CO}_2$  by wetland plants and carbon is generated in wetland system through the decay of biomass that, in part, generates methane ( $\text{CH}_4$ ) gas. Other carbon-rich compounds exist as soluble or insoluble and suspended as particulate forms. The molecular forms of these compounds are both organic or inorganic in nature, dissolved or suspended, solid or gaseous, as well as volatile. Of all of the carbon compounds in a wetland, the majority are organic in molecular form. Analytical methods have been generated by which each of these various

forms of carbon can be determined. The following table provides an overview of the analytical methods of carbon analysis.

| <b>Analytical Method</b>      | <b>Carbon Forms Analyzed</b>   |
|-------------------------------|--|
| Total Carbon (TC)             | All dissolved and suspended forms  |
| Particulate Carbon (PC)       | Organic and inorganic forms  |
| Dissolved Carbon (DC)         | Organic and inorganic forms  |
| Inorganic Carbon (IC)         | Dissolved and suspended forms including dissolved inorganic carbon consisting of $\text{CO}_2$ , $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ |
| Total Organic Carbon (TOC)    | Includes all dissolved and suspended forms including dissolved organic carbon and non-dissolved organic carbon                           |
| Volatile organic carbon (VOC) | Those carbonaceous species that have a low vapor pressure  |

**Table 12. Analytical methods of determining various forms of carbon.**

The measurement of the amount of organic material in the wetland is of primary concern. Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that is consumed by microbial organisms during an air-tight incubation. The analysis is conducted over a 5-day period, so in the literature or in regulatory reporting documentation one may see it represented as BOD<sub>5</sub>. Organisms that conduct nitrification may be present in the sample and therefore, at times, must be suppressed chemically to achieve a more accurate reading. When this chemical suppression is employed the result is commonly known as carbonaceous biochemical oxygen demand or CBOD<sub>5</sub>.

Chemical oxygen demand (COD) is a measurement of the amount of chemical oxidant required to oxidize the given organic matter in a sample. The oxidant utilized is potassium dichromate. This chemical test of carbon content of the water sample is much stronger than the microbial BOD test resulting in more carbon compounds being oxidized and therefore COD almost always has higher values than BOD.



**Method Summary:**

The measurement of BOD used standardized laboratory procedures to measure the relative oxygen requirements of the wetland samples. A sample of wetland water was removed and filled until overflowing in an airtight bottle. The airtight bottle was transported to the laboratory and placed in a BOD incubation bottle (VWR Labshop, Wheaton, 300 mL, <http://vwrlabshop.com/category.asp?c=6525&bhcd2=1165987735>). Dissolved oxygen (DO) was measured prior to incubation and after incubation. BOD was measured by computing the difference between the initial DO reading and the final DO reading. If samples were stored after collection, they were stored at or near freezing (4°C) for not more than 24 hrs. In general, samples were analyzed as soon as possible after collection. If samples were stored, they were warmed to 20°C prior to beginning the analysis. If storage was more than six hours, the temperature was reported at which the samples were stored and the length of time of storage was recorded.

**Apparatus:**

Incubation bottles (250-300ml capacity) and an incubator (air or water bath type) were used in this method. A water seal was used to prevent air from being drawn into the incubation bottle during incubation. This was accomplished by placing water in the flared mouth of the specially designed BOD bottles. The incubator was thermostatically controlled at 20°C ± 1°C. Incubation was kept out of the light so as to prevent photosynthetic production of DO.

**Reagents:**

*Phosphate buffer solution\** was prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> (8.5g), K<sub>2</sub>HPO<sub>4</sub> (21.75g), NaHPO<sub>4</sub>·7H<sub>2</sub>O (33.4g) and NH<sub>4</sub>Cl (1.7g) in distilled water (500 mL) in

volumetric flask (1 L). The solution was diluted to the mark and inverted to mix. The pH was buffered to 7.2 without further adjustment.

*Magnesium sulfate solution\** was prepared by dissolving  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (22.5g) in distilled water (500 mL) in a volumetric flask (1 L) and diluted to the mark. The solution was inverted to mix.

*Calcium chloride solution\** was prepared by dissolving  $\text{CaCl}_2$  (27.5g) in distilled water (500 mL) in a volumetric flask (1 L) and diluted to the mark. The solution was inverted to mix.

*Ferric chloride solution\** was prepared by dissolving  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.25g) in distilled water (500 mL) in a volumetric flask (1 L) and diluted to the mark. The solution was inverted to mix.

*Acid and alkali solutions* were prepared by dissolving  $\text{H}_2\text{SO}_4$  (28ml) in distilled water (500 mL) in a volumetric flask (1 L) and diluted to the mark and by dissolving  $\text{NaOH}$  (40g) in water (500 mL) in a volumetric flask (1 L) and diluted to the mark. The solutions were inverted to mix.

*Sodium sulfite solution* was prepared by dissolving  $\text{Na}_2\text{SO}_3$  (1.575g) in water (500 mL) in a volumetric flask (1 L) and diluted to the mark. The solution was inverted to mix. This solution is not stable and was prepared fresh daily.

*Nitrification inhibitor*, 2-chloro-6-(trichloromethyl) pyridine, Nitrification inhibitor 2579-24 (2.2% TCMP), Hach Co., or equivalent.

*Glucose-glutamic acid solution*: Glucose and glutamic acid were dried at  $103^\circ\text{C}$  for 1h. Glucose (150mg) and glutamic acid (150mg) were added to water (500 mL) in volumetric flask (1 L) and diluted to the mark. This solution was prepared fresh daily.

*Ammonium Chloride Solution\**: Ammonium chloride ( $\text{NH}_4\text{Cl}$ , 1.15g) was dissolved in water (500 mL) in a volumetric flask (1 L), pH was adjusted to 7.2 with NaOH solution. Solution was diluted to the mark. The solution contained 0.3 mg N/mL.

\*Nutrient Buffer Pillow was used in place of above chemicals in preparation of dilution water. BOD Nutrient Buffer Pillow (HACH Company, Loveland, CO cat # 14862-66) was dissolved in 6 liters of water.

***Procedure:***

Dilution water preparation – The volume of the dilution water needed was determined.  $\text{MgSO}_4$ ,  $\text{CaCl}_2$ , and  $\text{FeCl}_3$  (1 mg/L) were added to dilution water. Seed dilution water if needed (described in Seeding). DO of the dilution water was tested before the water was stored. Prior to use, dilution water was saturated with DO by shaking it in a partially filled bottle or sparging with organic free air.

Dilution water check – Dilution water should not exceed 0.2 mg/L BOD. If this level of DO is exceeded, the source was checked as well as the procedure and or glassware used in preparation. A sufficient amount of seeding material was added to measure DO. The BOD bottle full of dilution water was incubated for 5 days at 20°C. DO was measured at the end of incubation period. BOD was calculated. BOD should not exceed 0.2 mg/L in dilution water.

Glucose-Glutamic Acid Check – The 5-day 20°C BOD of a 2% dilution of glucose-glutamic acid standard check solution was determined under the same procedure as the dilution water check as outlined above.

Seeding and Seed Source – NOTE: Some wastewaters (extreme pH, disinfected wastes, high-temperature wastes) do not contain sufficient bacterial populations to

degrade the biological material in a sample. These wastewaters must be seeded. The wetland wastewater, as well as domestic wastewater, unchlorinated wastewater and surface waters receiving wastewater generally have sufficient populations of microorganisms to biodegrade material.

*Sample Collection and Pretreatment* - A one liter bottle was acid washed and filled with wetland water sample and placed in the refrigerator. Samples were neutralized to a pH between 6.5 and 7.5. Prepared concentrated reagents were used to minimize the affects of dilution. Dilution should not be more than 0.5% of the sample.

NOTE: Samples with supersaturated DO – samples containing more than 9 mg DO/L at 20°C are generally encountered in cold waters or in waters where photosynthesis occurs. Loss of DO can be prevented by bringing samples to 20°C under vigorous shaking or by aeration with clean filtered compressed air. Wetland samples were not supersaturated with DO.

Before dilutions, bring sample temperature to 20°C ± 1°C.

Nitrification inhibition can be conducted by adding 3 mg of TCMP to each incubator bottle before capping.

Prepare dilutions accordingly.

*Determination of initial DO* - See DO determination method.

*Dilution water blank* – a dilution water blank was prepared using DI water diluted in the same fashion as each sample.

*Incubation* – BOD bottles containing desired dilutions, seed controls, dilution water blanks and glucose-glutamic acid checks were incubated.

*Determination of Final DO* – After five days, DO was determined of all samples, blanks and checks.

**Calculations:**

When dilution water is not seeded the following equation with BOD units in mg/L was used:

$$\text{BOD}_5 = D_1 - D_2/P \quad (6.1)$$

When dilution water was seeded, the following equation with BOD units as mg/L was used:

$$\text{BOD}_5 = (D_1 - D_2) - (B_1 - B_2) * f/P \quad (6.2)$$

Where:

$D_1$  = DO of diluted sample immediately after preparation, mg/L.

$D_2$  = DO of diluted sample after the 5-day incubation at 20°C, mg/L

$P$  = decimal volumetric fraction of sample used

$B_1$  = DO of seed control before incubation, mg/L

$B_2$  = DO of seed control after incubation, mg/L

$f$  = ratio of seed in diluted sample to seed in seed control = (% seed undiluted sample)/(% seed in seed control).

If seed material is added directly to sample or to seed control bottles, then

$f$  = (volume of seed in diluted sample)/(volume of seed in seed control)

### **6.2.0 Total Suspended Solids**

**Background:**

Wetland water concentration of total suspended solids (TSS) is determined gravimetrically after filtration and drying a known sample of wetland water. Care must

be taken in the sampling so as not to disturb the wetland detritus material which may significantly skew the results of the analysis.

**Introduction:**

A known volume of a thoroughly mixed sample was filtered through a pre-weighed filter paper. The filter and residue on the filter were then dried at 103°C – 105°C and mass measured to a constant weight (dry time ~2 hrs, with cool time ~1 hr). Non-homogenous or large floating particles were minimized or removed from the filter or sample. Sample volume was limited so the potential TSS was not more than 200 mg/L. Filter paper was thoroughly rinsed with samples containing high dissolved solids. Colloidal particles may be trapped within the filter during long filter times. Filter time was minimized to prevent this interfering affect.

**Apparatus:**

Equipment included a drying oven, dessicator, aluminum weighing boats, filter paper (1.2 micron), filter funnel, graduated cylinder, vacuum flask, and tweezers.

**Procedure:**

The TSS wetland sample was collected in a 250 mL plastic bottle. (When convenient and for efficiency, the TSS sample was removed from another analytical sample such as BOD or nitrate/nitrite.) The wetland sample was thoroughly shaken to suspend any settled solids. A known volume was removed (50-100mL) and measured with a graduated cylinder. Known sample volume was passed through the pre-weighed filter paper via the filter funnel and into the vacuum flask. The filter paper was removed and placed back in weighing boat and dried (2hrs at 103°C – 105°C) to constant mass. Calculation of TSS in units of mg/L:

$$\text{TSS} = ((A-B) \times 1000)/\text{sample volume} \quad (6.3)$$

where:

A = weight of filter and dried residue (mg)

B = weight of filter, (mg)

### **6.3.0 Nitrogen**

#### **6.3.1 Ammonia**

##### **Background:**

There are a number of ways to determine ammonia in water. The selection of the most effective method is determined by the concentrations of ammonia in the sample to be analyzed and the presence of interferences (91). For the determination of ammonia in the wetland samples the method employed by the Missoula WWTP was adopted. The following is an overview of this method.

##### **Summary:**

The determination of ammonia was performed based on the Berthelot reaction where ammonia was reacted with alkaline phenol, followed by sodium hypochlorite to form indophenol blue. The absorbance of indophenol blue was measured at 630 nm with this reaction product directly proportional to the ammonia concentration found in the original sample. Sodium nitroprusside was added to increase the sensitivity (92).

##### **Interferences:**

If present in sufficient concentrations, Ca and Mg ions may precipitate. This was managed through the addition of tartrate or EDTA buffers. Color or turbidity and certain organic species may cause interferences. Filtration solved any turbidity interferences that were experienced. The wetland samples did not have any color issues.

#### Equipment and Supplies:

- 1) Balance – an analytical balance capable of accurately weighing samples to the nearest 0.0001g.
- 2) Volumetric flasks (Class A) and pipettes and other plastic containers as required. Samples can be stored in plastic or glass
- 3) Flow injection analysis equipment capable of delivering and reacting samples with reagents in the requisite orders and ratios.
  - a. Sampler
  - b. Multichannel proportioning pump
  - c. Reaction unit or manifold
  - d. Colorimetric detector
  - e. Data systems with PC system or software interface
- 4) Heating unit

#### Reagents and Standards:

Deionized water was used in the preparation of all reagents and standards and degassed as necessary by bubbling with Helium.

##### Reagent 1. Sodium Phenolate

CAUTION: Gloves were worn as phenol causes burns and readily absorbed through the skin.

Crystalline phenol ( $\text{C}_6\text{H}_5\text{OH}$ , 83 g) was added to water (600 mL) in a volumetric flask (1 L). Phenol was dissolved, allowed to cool, and the solution was diluted to the mark and inverted to mix. This solution was not degassed.

##### Reagent 2. Sodium Hypochlorite



Regular Clorox bleach (5.25% sodium hypochlorite ( $\text{NaOCl}$ ), 250 mL), was added to a volumetric flask (500 mL) and diluted to the mark with DI water. The solution was inverted to mix.

#### Reagent 3. Buffer

Disodium ethylenediamine tetracetate ( $\text{Na}_2\text{EDTA}$ , 50.0 g) and sodium hydroxide ( $\text{NaOH}$ , 5.5 g) were dissolved in water (900 mL) in a volumetric flask (1 L). The solution was diluted to the mark and mixed with a magnetic stirrer until dissolved.

#### Reagent 4. Sodium Nitroprusside

Sodium nitroprusside (Sodium nitroferrocyanide ( $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ ), 3.50 g) was added to water (600 mL) in a volumetric flask (1 L), diluted to the line and inverted to mix.

#### Preparation of Standards:

##### Standard 1. Stock Standard 1000 mg $\text{NH}_3$

Ammonium Chloride ( $\text{NH}_4\text{Cl}$ , 4.6368 g), dried for two hours at  $110^\circ\text{C}$ , was dissolved in water (800 mL) in a volumetric flask (1 L), diluted to the mark and inverted to mix.

##### Standard 2. Intermediate Stock Standard 50 mg N/L

Standard 1 (50.0 mL) was added to a volumetric flask (1 L) and diluted to the mark with DI water. The solution was inverted to mix.

#### Working Standards:

The following working standards were prepared weekly by diluting the required amount of stock standard (Standard 1) and intermediate stock standard (Standard 2) in a volumetric flask (250 mL).

|  |        |        |        |       |       |       |       |       |       |      |
|--|--------|--------|--------|-------|-------|-------|-------|-------|-------|------|
| Working Standards<br>(prepared weekly)<br>Concentration mg<br>NH <sub>3</sub> /L | A      | B      | C      | D     | E     | F     | G     | H     | I     | J    |
|  | 30.000 | 20.000 | 10.000 | 8.000 | 2.000 | 1.000 | 0.400 | 0.200 | 0.100 | 0.00 |
| Volume of Standard 2<br>diluted to 250 mL w/<br>DI water.                        | 150    | 100    | 50     | 40    | 10    | 5     | 2     | 1     | 0.5   | 0    |

**Table 13. Working standards for ammonia analysis.**

**Sample Collection, Calibration and Standardization:**

In practice, each wetland sample required two acid washed sample bottles (250 mL), one for the field sample and one for storing the sample. Samples were filtered and a second sample bottle was thoroughly rinsed with a portion of the filtrate prior to the entire sample being added to storage bottle. Filtered samples were preserved to a pH of 2 with concentrated sulfuric acid.

The series of standards were prepared as outlined above. The instrument was calibrated by injecting the standards with the data system preparing a standard curve based on the instrument responses against each standard. After the calibration curve was established, it was verified via a suitable quality control standard with a +/-10% recovery of the established value of the quality control standard.

**Data Analysis and Calculations:**

Sample concentrations were calculated using the data from the system's calibration curve. The sample concentration was calculated from the generated regression equation. The results were reported in mg N/L.

### **6.3.2 Nitrate/Nitrite**

**Introduction:**

Determination of nitrate and nitrite in the wetland water was determined based on the chemistry of nitrite ion. In summary, nitrate is reduced quantitatively to nitrite utilizing a copper-cadmium column. By passing nitrate rich sample through this column the nitrate was reduced to nitrite plus the original nitrite in the sample. Nitrite was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The reaction product was a water soluble dye with a magenta color that was read at 520 nm. By removing the copper-cadmium column, nitrite was determined alone (93).

**Interferences:**

The copper-cadmium column may be oxidized by residual chlorine. Interference or low results may be realized with samples containing high concentrations of metals. EDTA was added within the buffer to mitigate this potential interference. While not an issue with the wetland water, samples known to contain large concentrations of oil and grease should be first extracted with an organic solvent as the surface of the column may become coated. Turbidity may interfere and, as such, all samples were filtered through a 0.45  $\mu$ m membrane prior to analysis.

**Safety:**

Standard precautionary laboratory practices were exercised while conducting this method. Bodily contact with reagents and samples was minimized.

**Equipment List:**

Analytical balance with accuracy to the nearest 0.0001g. Class A volumetric flasks and pipettes. Plastic may be and was used. Flow injection analysis equipment including an autosampler, multichannel proportioning pump, a reaction unit or manifold,

the colorimetric detector and a data collection system. Special equipment included the column (Lachet Part No. 50230).

### **Reagents and Standards:**

Deionized water (10 megohm) was used for all solutions. All solutions, except the standards, were degassed with helium.

#### **Reagent 1. 15 N Sodium Hydroxide**

Sodium hydroxide (NaOH, 150 g) was added to water (250 mL). CAUTION: The solution got very hot, so water was add slowly. The solution was stirred and swirled until NaOH dissolved. The solution was allowed to cool and stored in a plastic bottle.

#### **Reagent 2. Ammonium Chloride Buffer, pH 8.5**

Ammonium chloride (NH<sub>4</sub>Cl, 85 g) and disodium ethylenediamine tetracetic acid dihydrate (Na<sub>2</sub>EDTA-2H<sub>2</sub>O, 1.0 g) was added to water (938 g). The solution was stirred until dissolved and then pH adjusted to 8.5 with the 15 N NaOH solution. Note: Ammonium chloride (ACS grade) has been found to contain nitrate contamination. As such the alternative method was utilized:

CAUTION: Fumes! This was prepared in a hood. Water (500 mL) was added to a volumetric flask (1 L) to which was slowly added concentrated hydrochloric acid (HCl, 95 mL), ammonium hydroxide (NH<sub>4</sub>OH, 95 mL), and disodium EDTA (1 g). The solution was dissolved, diluted to mark, inverted to mix, and adjusted to pH of 8.5 with an HCl or 15 N NaOH solution.

#### **Reagent 3. Sulfanilamide color reagent**

Water (600 mL) was added to a volumetric flask (1 L). Phosphoric acid (85%, 100 mL, H<sub>3</sub>PO<sub>4</sub>), sulfanilamide (40.0 g), and N-(1-naphthyl)ethylenediamine

dihydrochloride (NED, 1.0 g) were added. The solution was stirred for 30 min until dissolved, diluted to the mark, inverted to mix and stored (stable for 1 month) in a dark bottle.

### **Preparation of Standards:**

Standard 1. Stock Nitrate Standard 100.0 mg N/L as  $\text{NO}_3^-$

Potassium nitrate ( $\text{KNO}_3$ , 0.722 g) was added to water (600 mL) in a volumetric flask (1 L). Chloroform (2 mL) was added and the solution was diluted to the mark, inverted to mix, and stored (stable for approximately 6 months).

Standard 2. Working Nitrate Standard, 1.00 mg/L as  $\text{NO}_3^-$

Stock Standard 1 (10.00 mL) was added to a volumetric flask (1 L). The solution was diluted to mark with water and inverted to mix.

Standard 3. Stock Nitrate Standard, 100.0 mg N/L as  $\text{NO}_2^-$

Sodium nitrite ( $\text{NaNO}_2$ , 0.493 g) was dissolved in water (800 mL) in a volumetric flask (1 L). The solution was diluted to the mark with water and inverted to mix. This solution was refrigerated.

Standard 4. Working Nitrite Standard, 1.00 mg N/L as  $\text{NO}_2^-$

Standard 3 (10 mL) was added to a volumetric flask (1 L). The solution was diluted to the mark with water and inverted to mix.

Working Standards: The following were prepared daily on test or analysis day from stock standard solutions.

|  |            |           |           |           |           |           |           |
|--|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Working Standards<br>Concentration $\mu\text{g N/L as NO}_3^-$       | A<br>100.0 | B<br>50.0 | C<br>25.0 | D<br>10.0 | E<br>5.00 | F<br>2.00 | G<br>0.00 |
| Volume (mL) of working standard 2<br>diluted to 250 mL with DI water | 25.0       | 12.5      | 6.25      | 2.50      | 1.25      | 0.50      | 0.00      |

|   |            |           |           |           |           |           |           |
|---|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Working Standards<br>Concentration $\mu\text{g N/L as NO}_2^-$                | A<br>100.0 | B<br>50.0 | C<br>25.0 | D<br>10.0 | E<br>5.00 | F<br>2.00 | G<br>0.00 |
| Volume (mL) of working stock<br>standard 4 diluted to 250 mL with DI<br>water | 25         | 12.5      | 6.25      | 2.50      | 1.25      | 0.50      | 0.00      |

**Table 14. Working standards for nitrate/nitrite analysis.**

**Sample Collection and Preservation:**

In practice, each wetland sample required two acid washed sample bottles (250 mL) - one bottle for the field sample and one bottle for storing the sample. Samples were filtered and the second sample bottle was thoroughly rinsed with a portion of the filtrate prior to entire sample being added to storage bottle. Filtered samples were preserved to a pH of 2 with concentrated sulfuric acid. Samples were stored for up to 28 days.

**Quality Control:**

Quality control was demonstrated through the use of reagent blanks, fortified blanks, and other performance checks. Instrumentation performance was the first step in this quality control methodology and utilized a linear calibration range established through the analysis of quality control samples. This was followed by determination of laboratory performance by using the method detection limit (MDL). The laboratory at the Missoula wastewater treatment plant periodically calculated (at least every 6 months) the linear calibration range (LCR), or the concentration range over which the instrument response is linear. The determination of the LCR used sufficient standards including a minimum of a blank and three standards. A tolerance range for verification of data was

set at +/- 10%, and sufficient standards were used to define the non-linear portion. Every sample run included a quality control sample (QCS). The QCS was a solution of method analytes of known concentrations that was used to spike the laboratory reagent blank (LCR). The LCR was an aliquot of reagent water or other blank matrices that was digested exactly as the samples including exposure to all glassware, equipment, and reagents that were used with the other samples. The blank indicated the presence or lack of interferences in the method analytes or other interferences within the laboratory, reagents, or the apparatus. The method detection limit (MDL) was established for all analytes, using the reagent water (blank) with a concentration added at two to three times the instrument detection limit. Seven replicate aliquots of the fortified reagent water were taken through the entire method. The MDL is calculated by:

$$MDL = t \times S \quad (6.4)$$

where, t is the Student's t value for a 99% confidence (t = 3.14 for seven replicates) and a standard deviation estimate with n-1 degrees of freedom, where S is the standard deviation of the replicate analyses. The MDL was determined by the Missoula WWTP at least every six months, upon a change of operator or change in instrument response.

The performance of the laboratory is conducted with a laboratory reagent blank, the "blank". A blank was used with each batch of samples analysed. This blank assesses contamination from the laboratory environment. The performance of the laboratory is also assessed using a laboratory fortified blank (LBF) or the control. If the percent recovery of any analyte fell outside the required control limits of 90-110%, then the

analyte was judged as out of control and the issues were determined and resolved. During the process of running a series of samples a Instrument Performance Check Solution (IPC) or check standard was used. This is a mid-range check standard that was employed after every tenth sample and at the end of the sample run. The IPC must verify that the instrument was within +/- 10% of calibration. If the calibration cannot be verified then the IPC was re-analyzed. If upon re-analysis, the IPC solution was outside the limits, then the analysis was discontinued, the cause determined and in the case of drift, the instrument recalibrated. If the check standard fell outside the acceptable limits then all the samples following the last acceptable check standard were reanalyzed. All of the analysis data was printed out with the test results generated by the analysis software.

Data quality is assessed by investigating analyte recovery. A Laboratory Fortified Sample Matrix (LFM) or duplicate was used for this assessment. Basically a sample was spiked (fortified) with a known amount of added analyte at a know concentration. The percent recovery for each analyte, corrected for concentrations in the unfortified sample, was calculated and recovered in the 90-110% range. Percent recovery was calculated using the following equation:

$$R = [(C_s - C)/s] \times 100 \quad (6.5)$$

With R being the percent recovery,  $C_s$  is the fortified sample concentration, C is the sample background concentration, and s is the concentration equivalent of analyte added to the sample. If the recovery was outside the designated range and the laboratory performance was shown to be in control from the laboratory reagent blank and laboratory spike (as discussed above), then the recovery problem was either matrix or solution



related rather than system related. Overall all, when available, reference materials were used in the analysis to provide additional performance data.

#### **Calibration and Standardization:**

Calibration and standardization was conducted by preparing a series of standards as discussed above, through dilution of the appropriate stock solution. The instrument was properly set up and parameters input into the software. DI water was pumped through all reagent lines to detect leaks or for smooth flow. System was then switched to reagents and allowed to equilibrate to a stable baseline. Standard samples were placed into the autosampler and analysis initiated utilizing the software. The software prepared a curve by plotting the instrument response against concentration values within set acceptable control limits. The curve was then checked with a suitable quality control sample (QCS) with a target range of +/- 10% of the known QCS value. The curve was continuously checked via periodic re-analysis of the QCS sample.

#### **Data Analysis and Calculations:**

With the calibration curve established and checked, the sample concentration was checked using a regression equation. Samples that fell outside of the lowest and highest values of the calibration curve were diluted and reanalyzed. All data was reported at mg/L.

### **6.3.3 Total Kjeldahl Nitrogen**

#### **Introduction:**

Total Kjeldahl Nitrogen (TKN) was determined by block digestion method with the colorimetric flow injection analysis as approved by 40 CFR Part 136. The method outlined below was adopted from a QuikChem Method 10-107-06-02-D published by

Lachat Instruments (94). This method covers the determination of TKN in drinking water, ground, and surface waters, domestic and industrial wastewaters. Nitrogen containing biological compounds such as amino acids, proteins, and peptides are converted to ammonium ion ( $\text{NH}_4^+$ ). Nitrate nitrogen and other amines, nitro compounds, hydrazones, oximes, and semi-carbazones are not converted to ammonia. This discussion is based on high level TKN analysis (1-40 mg/L).

**Summary:**

Unknown samples, blanks, spikes and standards to be analyzed (50 mL) were added to digestion flasks (250 mL). Digestion samples containing the unknown were then diluted with digestion solution (67 g  $\text{K}_2\text{SO}_4$ , 3.65 g of  $\text{CuSO}_4$  and 67 mL of  $\text{H}_2\text{SO}_4$  diluted to 500 mL) and heated on a digestion block at 180°C for 90 minutes then at 380°C for 80 minutes. Boiling chips were added to even out the boiling and prevent bumping. Cold fingers were placed on each flask to help contain fumes and provide consistency with the flask. The remaining residue was allowed to cool, rehydrated with water (50 mL) and analyzed for ammonia.

TKN was measured as the sum of ammonia and organic nitrogenous compounds that were converted to ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) during the digestion process. Known and unknown samples were arranged in a Lachat auto sampler series ASX-500 and injected into the chemistry manifold (board) of the Lachat auto analyzer via a Lachat Reagent Pump (40 rpm). Data analysis was conducted from a PC platform using an Omnion FIA Data system.

Approximately 0.3 mL of the sample (digested) was injected into the board where the pH was controlled and raised to a known basic pH by neutralization with a

concentrated buffer (450 mL distilled H<sub>2</sub>O, 450 mL potassium sodium tartrate, D,L-NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O, 25 g NaOH, and 13.4 g of sodium phosphate dibasic heptahydrate, Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O diluted to 500mL). The effect of this neutralization was the conversion of the ammonium cation to ammonia and also to assist in prevention of the sulfuric acid matrix influence on the pH-sensitive color reaction.

The ammonia produced was heated with salicylate solution (75 g sodium salicylate [salicylic acid sodium salt, C<sub>6</sub>H<sub>4</sub>(OH)(COO)Na], 0.5 g of sodium nitroprusside [sodium nitroferricyanide dihydrate, Na<sub>2</sub>Fe(CN)<sub>5</sub>NO·2H<sub>2</sub>O] diluted to 500 mL) and hypochlorite (15 mL of Regular Clorox Bleach diluted to 250 mL) which produces a blue color that is proportional to the ammonia concentration. Sodium nitroprusside intensifies the blue color and EDTA in the buffer solution prevents precipitation of calcium and magnesium.

### **Interferences**

Digestion samples did not consume more than 10% of the H<sub>2</sub>SO<sub>4</sub> during the digestion process. The buffer was designed to accommodate 4.5-5.5% (v/v) H<sub>2</sub>SO<sub>4</sub> in the diluted digestion sample with no change in intensity.

High nitrate samples (10X or more than the TKN level) generate low TKN values. Samples were diluted if interference occurred. Digest must be free of turbidity.

### **Equipment and Supplies:**

- 1) Balance – Analytical, capable of weighing to the nearest 0.0001 g.
- 2) Glassware – Class A volumetric flasks and pipettes or plastic containers as required.
- 3) Sampler

- a. Multi-channel proportioning pump
  - b. Reaction unit or manifold
  - c. Colorimetric detector
  - d. Data System
  - e. 10 nm band pass, 80  $\mu$ L, glass flow cell
  - f. 660 nm interference filter
- 4) Helium degassing tube
  - 5) Heating Unit
  - 6) Block Digester (BD-26)/250 mL tubes
  - 7) Pipets
  - 8) Vortex Mixer

**Reagent Summary:**

Distilled H<sub>2</sub>O was used for all solutions.

**Reagent 1. Digestion Solution**

67 g K<sub>2</sub>SO<sub>4</sub>, 3.65 g of CuSO<sub>4</sub> and 67 mL of H<sub>2</sub>SO<sub>4</sub> diluted to 500 mL. The solution was inverted to mix. The solution was prepared fresh monthly.

**Reagent 2. Buffer**

450 mL distilled H<sub>2</sub>O, 450 mL potassium sodium tartrate, D,L-NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O, 25 g NaOH, and 13.4 g of sodium phosphate dibasic heptahydrate, Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O were added to a volumetric flask (500 mL) and diluted to the mark. The solution was inverted to mix.

**Reagent 3. Sodium Hydroxide (0.8M)**

Sodium Hydroxide (NaOH, 32 g) was dissolved in water (800 mL) in a volumetric flask (1 L) and diluted to the mark. Solution was inverted to mix and prepared fresh monthly.

#### Reagent 4. Salicylate Nitroprusside

Sodium salicylate (salicylic acid sodium salt,  $C_6H_4(OH)(COO)Na$ , 75 g), sodium nitroprusside [sodium nitroferrocyanide dihydrate,  $Na_2Fe(CN)_5NO \cdot 2H_2O$ , 0.5 g] was dissolved in water (450 mL) in a volumetric flask (500 mL) and diluted to the mark. Solution was inverted to mix and prepared fresh monthly.

#### Reagent 5. Hypochlorite Solution

Regular Clorox Bleach (5.25% sodium hypochlorite, 15 mL) was added to a volumetric flask (500 mL) and diluted to the mark. Solution was inverted to mix and prepared fresh daily.

#### Sample Collection:

Samples were collected in thoroughly cleaned acid washed bottles (250 mL) and preserved with approximately 2 mL of concentrated sulfuric acid. The samples were analyzed within 30 days.

#### Standard Preparation:

TKN standard stock solution was prepared by dissolving 1.0504 g of glutamic acid (1.0504 g) in water (1 L) for a 100 ppm solution. From this stock solution dilutions were made for standards from 1 to 40 ppm. Inserted below is a table of dilutions and resultant standard concentration.

| From 100 ppm stock solution | Standard Concentration (ppm) |
|-----------------------------|------------------------------|
| 1 mL/100 mL                 | 1                            |
| 1 mL/50 mL                  | 2                            |
| 5 mL/100 mL                 | 5                            |

|             |    |
|-------------|----|
| 5 mL/50 mL  | 10 |
| 10 mL/50 mL | 20 |
| 20 mL/50 mL | 40 |

**Table 15. Dilutions and standards for TKN analysis.**

**Quality Assurance/Quality Control:**

The linear calibration of the standard curve was verified with the use of check standards from the standards used to build the standard curve. For TKN the 2 and 10 ppm standards were used as the check standards.

A laboratory reagent blank was used with each test to measure or assess the contamination from the laboratory environment.

A laboratory fortified blank was used with accuracy calculated as percent recovery within 90-110%. If this blank fell out of this range then the source of the problem was identified and resolved before continuing the analysis.

Check standards and a blank were analyzed after every 10 samples and at the end of every sample run. Verification was determined to be within +/-10%.

Results of blanks and check standards were kept on file with sample analysis data.

Analyte recovery was measured with the use of a spike. This provided assurance that the sample did not contain any inhibitors for accurate analysis of sample set.

The standard curve was prepared by plotting instrument responses against concentration values of standards.

**Digestion Procedure:**

Both standards and samples were digested in tubes. To 50 mL of sample was added 20 mL of digestion solution using an acid resistant pipet. Boiling chips (Hengar granules 2-4 or 10-12 teflon stones) were added to each tube. Tubes were placed in the

preheated block heater for 1 hour at 160°C. After water boiled off cold fingers were placed (for use in model BD-26) on tubes. Digest was continued for 1.5 more hours, including ramp time, with temp controller at 380°C maintained at least 30 minutes.

Samples were removed from the block and allowed to cool (5-10 minutes) and re-hydrated with 20 mL of water. A volumetric addition of re-hydrate water was used.

#### **System Start-Up:**

Calibration curve was established and checked. DI water was pumped through the system to check for leaks and smooth flow and pump was switched to reagents and system was allowed to equilibrate for a stable baseline. With standards in the sampler, sample tray full, and replicates and QC scheme established the sampler was started and analysis initiated.

#### **Data Analysis and Calculations:**

Sample concentration was computed by the software interface with the instrumentation by comparing the instrumentation response against the calibration curve. The results were reported in mg TKN/L.

### **6.4.0 Phosphorus**

Phosphorus is found in natural waters and in wastewaters primarily as phosphates which are classified into three groups; orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. These compounds of phosphorus are found in the various structural features of the water or wastewater such as in solution, in suspended particles, detritus or in aquatic organisms.

The City and County of Missoula has banned the use of detergents that contain phosphate. Other sources of phosphate in the wastewater include boiler water from industrial sites and from body wastes and food residues (91).

Phosphorus was analyzed as total phosphorus and as orthophosphorus. The methods of each analysis are described below.

#### **6.4.1 Total Phosphorus**

##### **Summary:**

Wetland samples were block digested with sulfuric acid. The phosphorus was converted to the orthophosphate anion with a mercuric oxide catalyst. Boiling temperature of the digestion was raised with potassium sulfate. Increasing the boiling temperature speeds the conversion to orthophosphate. The orthophosphate ion ( $\text{PO}_4^{3-}$ ) was reacted with molybdate and antimony potassium tartrate under acidic conditions. This reaction forms a complex which is subsequently reduced with ascorbic acid to form a blue complex with absorption of light at 880 nm with the absorbance being proportional to the concentration of orthophosphate in the sample (95).

##### **Interferences:**

Silica absorbs at 880 nm, but is generally insignificant as 4000ppm would be required to produce 1 ppm of error. Ferric iron at concentrations greater than 50 mg/L compete with the reaction complex for the reducing ascorbic acid and as such samples high in iron should be treated with sodium bisulfate. This was not an issue with the wetland water samples analyzed. Be sure to use special phosphate detergents in the laboratory and clean all glass ware with 1:1 HCl rinsed with DI water.

##### **Equipment and Supplies:**



- 1) Analytical Balance capable of accurately weighing to the nearest 0.0001g.
- 2) Class A volumetric flasks, pipettes, and plastic containers as necessary. (Samples may be stored in plastic or glass)
- 3) Flow injection analysis apparatus capable of delivering and reacting the samples and reagents in proper orders and correct ratios.
  - a. Autosampler
  - b. Multi-channel proportioning pump
  - c. Reaction unit or manifold
  - d. Colorimetric Detector
  - e. Data collection system or PC interface with software
  - f. Heating unit with block digester 75 mL (Lachat Part No. 1800-000)
  - g. 5 mL and 20 mL pipet dispensers
  - h. Vortex mixer

**Reagents and Standards:**

Deionized water was used for all solutions and all solutions were degassed, except for the standards, with helium. Degassing was accomplished by vigorously bubbling He through the solution for 1 minute.

**Reagent 1. Stock Mercuric Sulfate Solution**

Water (40 mL) was added to a volumetric flask (100 mL) along with 10 mL of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and mercuric oxide (8 g,  $\text{HgO}$ ). Mercuric oxide was stirred with low heat until dissolved. The solution was diluted to the mark and inverted to mix. This solution was stable for up to two months.

**Reagent 2. Digestion Solution**

Water (700 mL) was added to a volumetric flask (1 L) to which was added sulfuric acid ( $\text{H}_2\text{SO}_4$ , 200 mL). Potassium sulfate ( $\text{K}_2\text{SO}_4$ , 133 g) was added along with stock mercuric sulfate solution (reagent 1, 25 mL). The solution was diluted to the mark, mixed with a magnetic stirrer and allowed to cool. As necessary, solution was re-diluted to the mark after having cooled. This solution was prepared fresh on a monthly basis.

Reagent 3. Diluent 4.8% sulfuric acid (for simulated standards)

Water (600 mL) was added to a volumetric flask (1 L) followed by Reagent 2 (240 mL). The solution was diluted to the mark and inverted to mix.

Reagent 4. Stock Ammonium Molybdate Solution

Ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , 40.0 g) was dissolved in water (800 mL) in a volumetric flask (1 L). The solution was diluted to the mark and allowed to mix with a magnetic stirrer for at least four hours. This solution was stored and used for up to two months.

Reagent 5. Stock Antimony Potassium Tartrate Solution

In a volumetric flask (1 L) antimony potassium tartrate (3.0 g,  $\text{K}(\text{SbO})\text{C}_2\text{H}_4\text{O}_6\cdot 1/2\text{H}_2\text{O}$ ) was dissolved in water (800 mL). The solution was diluted to the mark, stirred with a magnetic stirrer until dissolved. The solution was stored in a dark bottle and used for up to two months.

Reagent 6. Molybdate Color Reagent

Water (500 mL) was added to a volumetric flask (1 L) to which was added reagent 4 (213 mL) and reagent 5 (72 mL). The solution was diluted to the mark, mixed by inverting, and degassed with helium. This solution was prepared weekly.

Reagent 7. Ascorbic Acid Reducing Solution

Ascorbic acid (60.0 g) was dissolved in water (700 mL) in a volumetric flask (1 L). Solution was diluted to the mark and mixed with a magnetic stirrer. The solution was degassed helium to which was added sodium dodecyl sulfate (1.0 g) and subsequently mixed with a magnetic stirrer. The solution was prepared fresh every two days.

#### Reagent 8. Sodium Chloride/Sodium Hydroxide Solution

Sodium Chloride (160 g) and sodium hydroxide (20 g) were dissolved in water (600 mL) in a volumetric flask (1 L). The solution was diluted to the mark and mixed with a magnetic stirrer. The solution was degassed with helium and prepared weekly.

#### Reagent 9. Sulfuric Acid/Potassium Sulfate Solution (Carrier)

5 mL of digestion solution was added to each sample of potassium sulfate ( $\text{K}_2\text{SO}_4$ , 31.7 g) and was dissolved in water (800 mL) in a volumetric flask (1 L). Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 50 mL) was added and diluted with water to the mark. The solution was mixed by inversion.

#### Reagent 10. Sodium Hydroxide – EDTA Rinse

Sodium Hydroxide ( $\text{NaOH}$ , 65 g) and tetrasodium ethylenediamine tetraacetic acid ( $\text{Na}_4\text{EDTA}$ ) was dissolved in 1.0 L of water. The solution was prepared monthly.

### **Preparation of Standards:**

#### Non-Digested Standards

##### Standard 1. Stock Standard 250.0 mg P/L

Standard grade anhydrous potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , 1.099 g) dried for 2 hours at  $110^\circ\text{C}$  was added to water (800 mL) in a volumetric flask (1 L) and diluted to the mark and inverted to mix.

Standard 2. Working Stock Standard Solution 5.00 mg P/L

Standard 1 (5.0 mL) was added to a volumetric flask (250 mL) and diluted to the mark with Reagent 3 (diluent). The solution was inverted to mix.

The table below represents the working standards that were prepared daily using Standard 2 and Reagent 3.

|  |           |          |          |          |          |          |         |         |        |
|--|-----------|----------|----------|----------|----------|----------|---------|---------|--------|
| Working Standards (Prepared Daily)<br>Concentration ug P/L             | A<br>1000 | B<br>800 | C<br>600 | D<br>400 | E<br>200 | F<br>100 | G<br>40 | H<br>20 | I<br>0 |
| Volume (mL) of Standard 2 that was<br>diluted to 250 mL with Reagent 3 | 50        | 40       | 30       | 20       | 10       | 5        | 2       | 1       | 0      |

**Table 16. Working standards for phosphorus analysis.**

Digested Standards

Standard 3. Working Stock Standard Solution 5.00 mg P/L

Standard 1 (5.0 mL) was diluted to mark in a volumetric flask (250 mL). The solution was inverted to mix.

The following table summarizes the standards that are digested.

|   |           |          |          |          |          |          |         |         |        |
|---|-----------|----------|----------|----------|----------|----------|---------|---------|--------|
| Working Standards (Prepared Daily)<br>concentration $\mu\text{g}$ P/L | A<br>1000 | B<br>800 | C<br>600 | D<br>400 | E<br>200 | F<br>100 | G<br>40 | H<br>20 | I<br>0 |
| Volume (mL) of Standard 3 that was<br>diluted to 250 mL with DI water | 50        | 40       | 30       | 20       | 10       | 5        | 2       | 1       | 0      |

**Table 17. Working standards that are digested for phosphorus analysis.**

**Sample Collection, Preservation and Storage:**

Samples were collected in thoroughly cleaned, rinsed and acid washed plastic bottles (250 mL). Samples were preserved by the addition of 2 mL of concentrated  $\text{H}_2\text{SO}_4$  per liter and stored at 4°C. This allowed for a holding time of not more than 28 days.

**Quality Control:**

The linear calibration of the standard curve is verified with the use of check standards from the standards used to build the standard curve. For the wetland samples the 4 and 8 ppm standards were used as the check standards.

A laboratory reagent blank was used with each test to measure or assess the contamination from the laboratory environment.

A laboratory fortified blank with accuracy calculated as percent recovery within 90-110%. If this blank falls out of this range then the source of the problem should be identified and resolved before continuing the analysis.

Check standards and a blank were analyzed after every 10 samples and at the end of every sample run. Verification was determined within  $\pm 10\%$ .

Results of blanks and check standards were kept on file with sample analysis data.

Analyte recovery is measured with the use of a spike. This provides assurance that the sample does not contain any inhibitors for accurate analysis of sample.

A standard curve was prepared by plotting instrument responses against concentration values.

**Calibration and Standardization:**

Nine standards were prepared between the concentrations ranges of 0 ppm to 10 ppm P. The instrument was calibrated by injecting the standards and the software in the data system generated a standard curve. Acceptable limits for the known concentrations of the standards and those represented by the curve were established at  $\pm 5\%$ . After

generation of a suitable curve it was verified by a quality control sample to within +/- 10% of known concentration.

### **Procedure:**

#### **Digestion Procedure.**

Both standards and samples were digested and if samples were preserved then the standards were preserved in a like manner. Digestion solution (5 mL, Reagent 2) was added to a sample (20 mL) in a digestion tube and mixed. Boiling chips were added. Tubes were placed in preheated (160°C) block digester for 1 hour. Water evaporated from the digestion tubes and cold fingers were placed on top of the sample tube. Samples were allowed to continue digesting for another 1.5 hrs with ramp of temperature to 380°C with 380°C temperature held for 30 minutes. Samples were removed from block and allowed to cool for 10 minutes. Water (20 mL) was added to each tube and mixed via vortex. Digestate was transferred to a clean labeled container.

### **System Start-Up Procedure:**

Calibration curve was established and checked. DI water was pumped through the system to check for leaks and smooth flow and pump was switched to reagents and system was allowed to equilibrate for a stable baseline. With standards in the sampler, sample tray full, and replicates and QC scheme established the sampler was started and analysis initiated.

### **Data Analysis and Calculations:**

Sample concentrations were computed by the software using the calibration curve against the sample response. Units were reported in mg/L.

## 6.4.2 Soluble Phosphorus

### Summary:

Soluble Phosphorus, otherwise known as the orthophosphate ion ( $\text{PO}_4^{3-}$ ) has similar analytical chemistry steps as total phosphorus. The orthophosphate ion was reacted with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. The complex was reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm with the absorbance being proportional to orthophosphate in the sample. Wetland samples were filtered using a 0.45 micron pore size filter providing only for the analysis of soluble phosphorus.

### Interferences:

Silica absorbs at 880 nm, but is generally insignificant as 4000 ppm would be required to produce 1 ppm of error. Ferric iron at concentrations greater than 50 mg/L compete with the reaction complex for the reducing ascorbic acid and as such samples high in iron should be treated with sodium bisulfate. This was not an issue with the wetland water samples analyzed. Be sure to use special phosphate detergents in the laboratory when and clean glass ware with 1:1 HCl rinsed with DI water.

### Equipment and Supplies:

- 1) Analytical Balance capable of accurately weighing to the nearest 0.0001 g.
- 2) Class A volumetric flasks, pipettes, and plastic containers as necessary. (Samples may be stored in plastic or glass)
- 3) Flow injection analysis apparatus capable of delivering and reacting the samples and reagents in proper orders and correct ratios.
  - a. Auto-sampler

- b. Multi-channel proportioning pump
- c. Reaction unit or manifold
- d. Colorimetric Detector
- e. Data collection system or PC interface with software
- f. Acid-washed glassware: All glassware that was used in this method was washed with 1:1 HCl and rinsed with DI water. Glassware was generally only used for this the method. Commercial detergents were not used.

### **Reagents and Standards:**

Deionized water was used for all solutions. Carrier solution was degassed with helium by bubbling for one minute.

#### **Reagent 1. Stock Ammonium Molybdate Solution**

Ammonium molybdate tetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ , 40.0 g] was dissolved in water (800 mL) in a 1 L volumetric flask and diluted to the mark. This solution was used for up to two months when stored under refrigeration.

#### **Reagent 2. Stock Antimony Potassium Tartrate Solution**

Antimony potassium tartrate  $(\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O})$ , 1.5 g) was dissolved in water (400 mL) in a volumetric flask (1 L). The solution was diluted to the mark and inverted to mix. The solution was stored in a dark bottle in the refrigerator. The solution was used for up to three months.

#### **Reagent 3. Molybdate Color Reagent**

Water (500 mL) was added to a volumetric flask (1 L). To this was added concentrated sulfuric acid (17.5 mL) while swirling the mixture. The solution increased in temperature upon addition of acid and once able to be handled, Reagent 2, (36 mL) and



reagent 1 (106.5 mL) were added. This solution was diluted to the mark and degassed with Helium. This solution was prepared fresh weekly.

**Reagent 4. Ascorbic Acid Reducing Solution, 0.33M**

Granular ascorbic acid (60.0g) was added to water (700 mL) in a volumetric flask (1 L). The solution was diluted to the mark. Dodecyl Sulfate ( $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ , 1 g) was added. This solution was prepared fresh weekly and discarded if it turned yellow.

**Reagent 5. Sodium Hydroxide – EDTA Rinse**

Dissolve Sodium Hydroxide (NaOH, 65 g) and tetrasodium ethylenediamine tetra acetic acid ( $\text{Na}_4\text{EDTA}$ , 6 g) in water (1 L).

**Preparation of Standards:**

**Standard 1. Stock Standard 250.0 mg P/L**

Primary standard grade anhydrous potassium phosphate monobasic ( $\text{KH}_2\text{PO}_4$ , 1.099 g) thoroughly dried for at least 1 hour at 105°C was added to water (800 mL) in a volumetric flask (1 L). The solution was diluted to the mark with DI water and inverted to mix.

**Standard 2. Working stock standard solution 5.00 mg P/L**

Stock standard 1 (5.0 mL) was added to a volumetric flask (250 mL) and diluted to the mark with DI water. The solution was inverted to mix.

**Working Standards:**

The following working standards were made using the following table as a guide.

| Standard working solution<br>mg P/L of solution                             | 7.00 | 5.00 | 2.00 | 1.00 | 0.50 | 0.20 | 0.10 | 0.00 |
|---|------|------|------|------|------|------|------|------|
| Volume of Standard 2 added to a<br>250 mL volumetric and diluted to<br>mark | 350  | 250  | 100  | 50.0 | 25.0 | 10.0 | 5.00 | 0.00 |

**Table 18. Working standards for soluble phosphorus analysis.**

**Sample Collections:**

Collection of this wetland sample requires two acid washed bottles (250 mL). One bottle was used for the field sample and one bottle was used to store the analytical sample. Samples were filtered immediately upon collection through 0.45 micron filter and storage bottle was rinsed with a portion of the filtrate prior to adding the total filtrate. Note: Filter paper may become clogged and, with care, filter paper can be removed and fresh filter paper used to facilitate large sample filtration.

**Quality Control:**

The linear calibration of the standard curve is verified with the use of check standards from the standards used to build the standard curve. For the wetland samples the 2.0 and 0.2 ppm orthophosphate standards are used as the check standards.

A laboratory reagent blank is used with each test to measure or assess the contamination from the laboratory environment.

A laboratory fortified blank with accuracy calculated as percent recovery within 90-110%. If this blank falls out of this range then the source of the problem should be identified and resolved before continuing the analysis.

Check standards and a blank are analyzed after every 10 samples and at the end of every sample run. Verification must be within +/-10%.

Results of blanks and check standards are kept on file with sample analysis data.

Analyte recovery is measured with the use of a spike. This provides assurance that the sample does not contain any inhibitors for accurate analysis of sample.

Standard curve is prepared by plotting instrument responses against concentration values.

**Calibration and Standardization:**

Using the table above, the series of working standards and a blank were used to prepare a standard curve by plotting instrument response against concentration values. This was done using a computer/software interface. After the curve was established it was verified by a suitable quality control standard targeting not less than  $\pm 10\%$  reading of the established quality control concentration value.

**Procedure:**

All samples were neutralized prior to analysis. With calibration and standardization complete, DI water was pumped through all the reagent lines to check for a smooth flow with no leaks. Samples were placed in the auto-sampler and testing initiated.

**Data Analysis and Calculations:**

Sample concentration was computed by the software interface with the instrumentation by comparing the instrumentation response against the calibration curve. The results were reported in mg P/L.

### ***6.5.0 Fecal Coliform***

**Summary:**

Fecal coliform was determined by the Membrane Filter Standard Method 9222D (91). Fecal coliforms are part of the total coliforms group and are an indicator of the presence of human feces in water. Fecal coliforms are defined as gram negative non-spore forming rods that ferment in lactose in  $24 \pm 2$  hours at  $44.5 \pm 0.20^\circ\text{C}$ . During

the fermentation process, the pH is lowered which causes a color change in rosilic acid, the pH sensitive acid that is used as an inhibitor in the culture media.

**Interferences:**

Heavy Metals

**Sample Handling and Preservation:**

Samples were collected in clean and sterile non-reactive borosilicate glass or suitable plastic bottles. Samples were collected using a pipette at various locations within the desired wetland cell. All sample pipettes were flushed utilizing aseptic techniques in order to avoid contamination. Samples were tested as soon as possible after collection and were frozen to  $<10^{\circ}\text{C}$  if analysis was unable to be performed in a timely manner.

**Matrices:**

Wetland water samples were taken at various locations in multiple 20 mL sample volumes.

**Instrument:**

A water bath able to be maintained at a temperature of  $44.5 \pm 0.20^{\circ}\text{C}$ .

**Equipment:**

Equipment includes the following:

- 1) Vacuum source
- 2) Sterilization oven
- 3) Vacuum Flask
- 4) Bunsen Burner
- 5) Sterile Petri dishes, 50x12 mm plastic

- 6) Sterile membrane filters, grid marked, 47 mm internal diameter with 0.45  $\mu$ m pore size
- 7) Forceps
- 8) 1-80 mL beaker
- 9) 1-2 L beaker
- 10) Watch glass
- 11) Hot Plate
- 12) Water bath dish for heating media (optional)
- 13) Pipet bulb

The following equipment was sterilized before use:

- 1) Stainless steel pipet container
- 2) Various glass pipets: 2-25 mL, 2-1 mL, 2-2 mL, 2-5 mL, 4-10 mL
- 3) 1-250 mL Erlenmeyer Flask
- 4) Glass or stainless steel membrane filter unit (filter base and funnel)
- 5) Glass with metal lid sample bottle with a minimum volume of 250 mL.
- 6) 1 L volumetric cylinder

**Reagents:**

- 1) MF-C Broth
- 2) Agar
- 3) Rosolic Acid
- 4) 0.20 N NaOH
  - a. 4 g NaOH in 500 mL of distilled water
- 5) 95% ethanol

6) Stock Buffer Solution 1

- a. In a 250 mL beaker add DI water (150 mL),  $\text{KH}_2\text{PO}_4$  (6.8 g), mix and bring pH to 7.2 with 1 N NaOH and dilute to 200 mL in a volumetric flask.

7) Stock Buffer Solution 2

- a. In a 250 mL beaker add DI water (200 mL),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , mix and dilute to 250 mL in a volumetric flask.

**Procedure:**

Samples were taken in the morning on designated days. All equipment was sterilized with all glassware being dry. Pipets were placed in a stainless steel pipet holder and openings on Erlenmeyer flask, volumetric cylinder and filter base and filter funnel were covered with aluminum foil and place in the oven. Uncovered sample bottles were also placed in the over utilizing an ovenproof tray. The tray and contents were heated to 350°F for 2 hours.

A 2 L beaker with 1200 mL of DI water, covered with a watch glass, was heated to a boil and boiled for not less than 2 minutes utilizing a Bunsen burner.

Water bath was turned on and allowed to warm to 44°C.

A 1% Rosolic acid solution was prepared in a glass stoppered bottle by adding 0.10 g of Rosolic acid with 10 mL of 0.20 N NaOH. Solution was mixed until acid dissolved.

Media was prepared by adding the following ingredients into a sterilized 250 mL Erlenmeyer flask:

| <b>Ingredients</b>        | <b>Amount</b> |
|---------------------------|---------------|
| MF-C Broth                | 5.55 g        |
| Agar                      | 2.25 g        |
| Distilled Water           | 150 mL        |
| 1 % Rosolic Acid Solution | 1.50 mL       |

**Table 19. Ingredient list for fecal coliform agar.**

The flask was covered with aluminum foil after the ingredients were added. The media was heated in a water bath to near boiling to dissolve the ingredients. Solution was stirred to ensure that ingredients did not stick to the side of the flask. Using a sterile 10 mL pipette with bulb, 5 mL of media were added to each Petri dish. Media was allowed to solidify for 30 minutes. Plates were used within 96 hours of preparation.

Buffer solution was prepared, using sterile pipettes, by adding 1.25 mL of stock buffer solution I ( $\text{KH}_2\text{PO}_4$ ) and 5 mL of stock buffer solution II ( $\text{MgSO}_4$ ) to a sterile 1 L volumetric and diluted to the mark with the cooled boiled water and inverted to mix.

**Test:**

Samples were collected and filtered. Care was taken not to touch the filter base where sample and sterile filter are placed. A small beaker was filled with 95 % ethanol and metal forceps were placed in the beaker. A known volume of sample was filtered through a sterile filter funnel and rinsed with 20 mL of buffer solution. Mixture was swirled and vacuum was turned on and sample was filtered. An addition 20 mL buffer rinse was conducted. Filter was removed with sterilized forceps and placed on appropriately labeled media plate while avoiding air entrapment under the filter paper. Process was repeated until all sample plates were prepared. Plates were placed in a sealable bag(s) and immersed in the water bath and incubated at temperature indicated for

24 +/- 2.0 hours. Plates were removed from the bag and blue circles (fecal coliform colonies) were counted. Two intersected colonies were counted as two coliform colonies. Colonies that were indistinguishable were recorded as too numerous to count (TNTC). Only those colonies that fall in the range of 20-60 colonies per plate were calculated.

**Calculations:**

The number of colonies per plate was recorded per volume of effluent used. The concentration was calculated to equal the number of colonies per 100 mL of sample. For example, if 1 ml of sample was used to on a plate and 35 colonies were counted then 35 was multiplied by 100 to 3500 colonies per 100 mL of sample.



## **7.0.0 Seasonal Treatment Analysis**

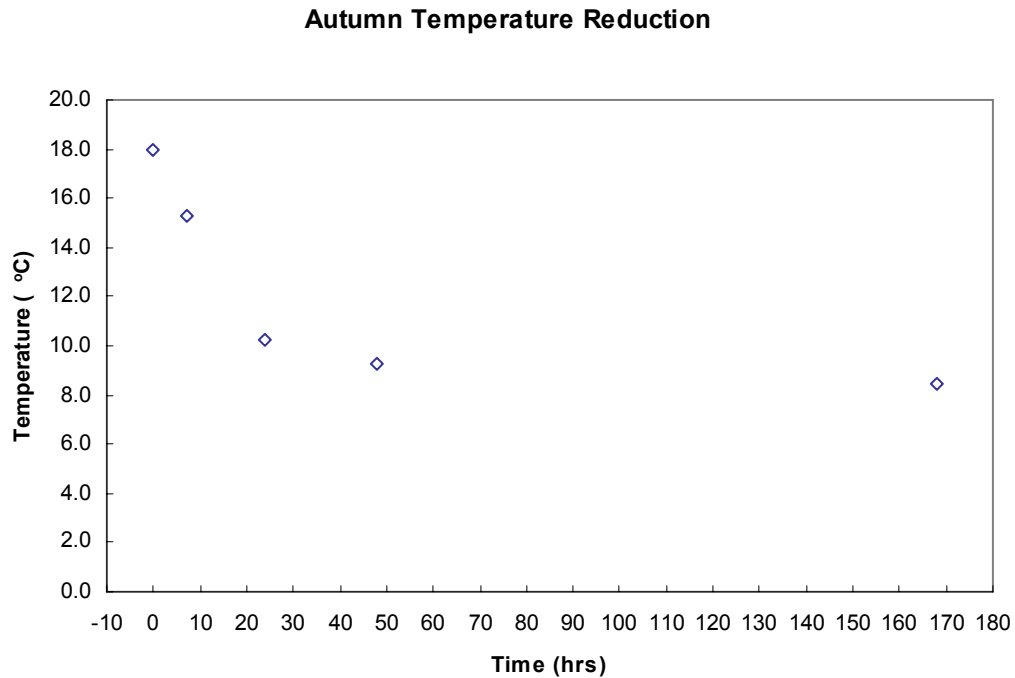
Constructed wetland treatment data was collected and separated into the four different seasons based on the temperature reduction of the water within the wetland system. This is described for each season below. For each season, data is presented for temperature, pH, COD, BOD,  $\text{NH}_4^+$ ,  $\text{NO}_3/\text{NO}_2$  and TKN.

### **7.1.0 Autumn**

#### **7.1.1 Temperature**

Temperature is very important in the determination of the seasons for the wetland treatment system. The autumn season is defined by a temperature reduction of between 40 and 60% between the primary effluent and the 7 day wetland effluent temperature. Below is plot showing the autumn temperature with respect to time. The data used to generate the plot was collected over two autumn seasons. The data was then averaged into an overall temperature with respect to time plot for autumn. The plot starts with the primary effluent being loaded (0 hour) to the wetland as the first data point and the last data point at the 168 hour (7 day) retention time, when the wetland effluent is discharged.

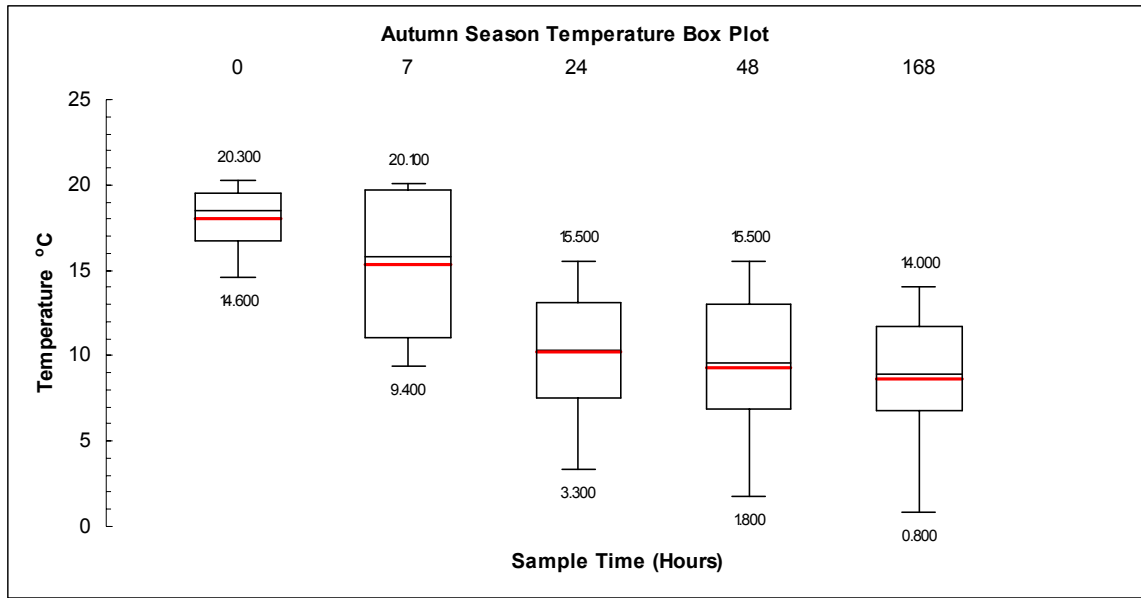
The seasonal data from which this plot is generated can be found in the Appendix E of this paper.



**Figure 31. Average wetland water temperature reduction plot for the Autumn season.** These data are for the Autumn season starting at time zero through a retention time of 168 hours.

As may be noted from the plot, the autumn season temperature reduction shows a rapid drop in temperature in the first 24 hours and stabilization within 48 hours of introduction of primary effluent to the wetland and a relatively constant temperature for the remainder of the retention time.

Below is a box plot showing the temperature reduction with respect to time for the autumn season.



**Figure 32. Box plot of the Autumn temperature reduction over 168 hour treatment cycle.** The sample times are from 0 through 168 hours and are labeled at the top of the plot.

The boxes for each sample time represent the middle fifty percent (50%) of the data for that particular sample time. The difference in the end of the whiskers is the range. No outliers can be seen on this particular plot. Outliers are marked with an open circle.

From this box plot these data suggest a gradual decrease in the temperature within the first 48 hours. This plot demonstrates how variable the temperature within the experimental constructed wetland system can be in autumn. There exists less variability over 50% of the data in the zero hour sample as compared to the other sample times.

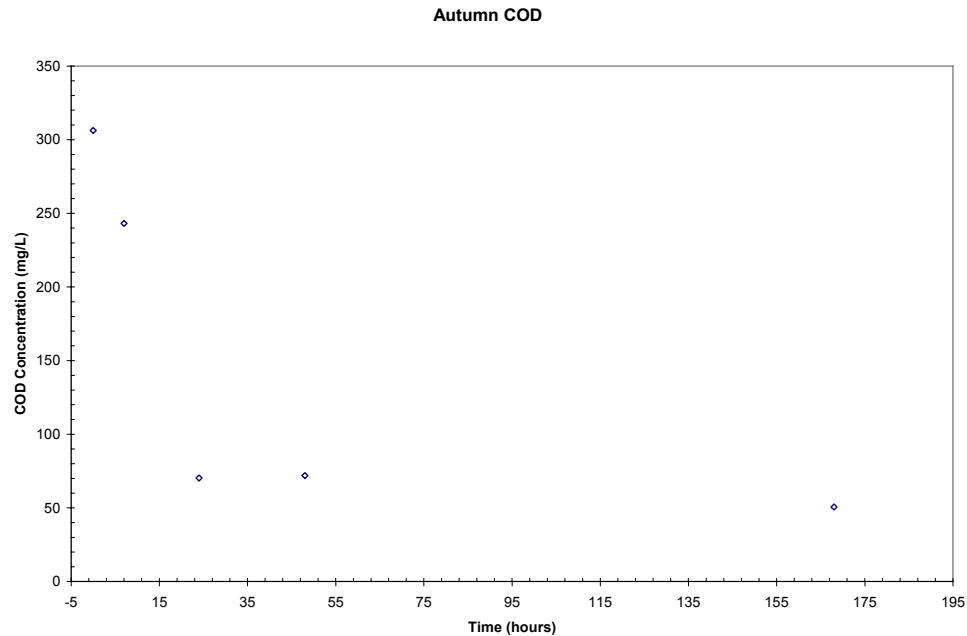
This is because the temperature of the wetland water at this time is being dominated by the primary effluent temperature being loaded into the wetland. These data also suggest increased variability over 50% of the data in the seventh hour sample as the ambient environmental conditions are gaining influence over the temperature of the system. At twenty four hours, after primary effluent introduction is discontinued and the recycle has been initiated, we see a wide range of temperatures with 50% of the data fairly

concentrated between eight and fourteen degrees Celsius. Fifty percent of the temperature data centered between 8°C and 14°C which persisted over the remainder of the treatment cycle. The range is quite large demonstrating the variability in temperature that this experimental system experienced during the autumn.

### **7.1.2 COD and BOD**

Chemical Oxygen Demand (COD) is defined as a measure of the oxygen equivalent to the organic matter in water based on reaction with a strong chemical oxidant (25). Autumn samples of COD were measured over time in a similar fashion as temperature in the previous section.

The following plot shows the average concentrations of COD plotted with respect to each hour in which samples were taken. As with the box plot and the previous individual experimental plots, these data suggest a definitive decrease in the concentration of COD within the first 24 to 48 hours with limited treatment after this time.

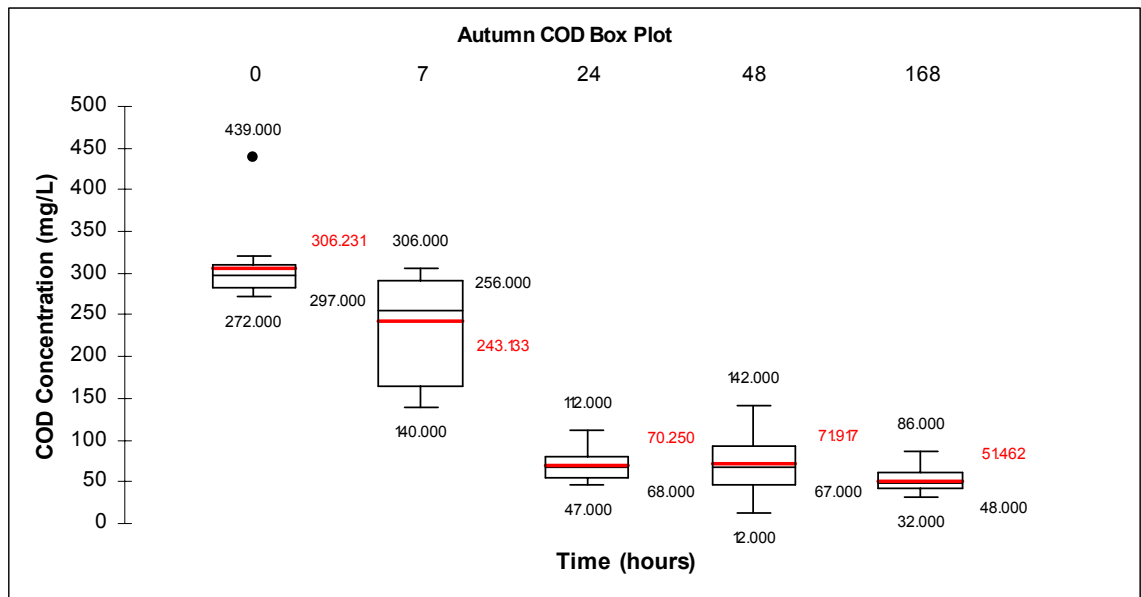


**Figure 33. Average wetland COD concentration (mg/L) reduction for Autumn season.** Data is plotted with respect to time (hours).

It is apparent that COD, during the autumn season, is rapidly treated in the constructed wetland within the first 24 to 48 hours. In addition, very little treatment is realized after 48 hours as the COD concentrations tend to stabilize and hold on the average between 50 to 70 mg/L.

The following box plot takes into account all of the autumn data for COD at each specific sample time. As may be noted in the zero hour the 439 mg/L COD concentration is considered an outlier within the data set. At the zero hour there exists a concentration of values around 50% of the data. Very little variability in COD was found at the zero hour over the course of the season. This is probably due to the zero hour being predominately influenced by the homogenous primary effluent. As the treatment of COD progresses over time we do see the anticipated drop in concentration over the 7 hour time period however 50% of the data are spread out over a wide range of values. A more

important note is that after 24 hours we see a narrowing of the data with a concentrated data set and a reasonable range. As expected in subsequent hours, under stabilized conditions, we find concentrated data sets with reasonable ranges at both 48 hours and 168 hours.



**Figure 34. Box plot of autumn COD data.** Samples were collected at hours 0, 7, 24, 48 and 168 hours after the introduction of primary effluent.

For these autumn COD data we find an 83% average reduction in COD over the course of the treatment cycle with most of this treatment occurring within the first 24 to 48 hours.

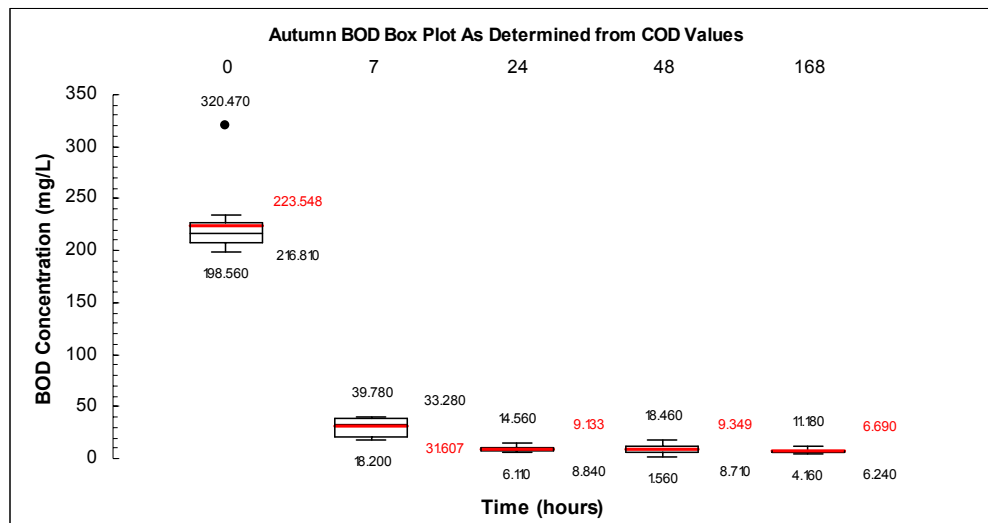
Similar to COD, Biochemical Oxygen Demand or BOD was measured.

Only the initial and final concentration of BOD was determined. Eight total BOD experiments were conducted in the fall of 2003. The table below represents the fall data for BOD reduction over each 168 hour treatment cycle.

| BOD (mg/L)  | 9/9/2003 | 9/23/2003 | 9/30/2003 | 10/7/2003 | 10/14/2003 | 10/21/2003 | 10/28/2003 | 11/4/2003 |
|-------------|----------|-----------|-----------|-----------|------------|------------|------------|-----------|
| Initial     | 166      | 231       | 175       | 171       | 168        | 163        | 160        | 174       |
| Final       | 10       | 5         | 5         | 2         | 2          | 4          | 5          | 4         |
| % Reduction | 94%      | 98%       | 97%       | 99%       | 99%        | 98%        | 97%        | 98%       |

**Table 20. Selected Autumn BOD initial and final concentrations.** These data were collected from the start dates of each 168 hour experiment during the autumn of 2003.

As these data suggest, the constructed wetland treatment system provides, in the autumn season, an average 97% reduction in the BOD concentration over 168 hours of treatment. COD can be used to estimate the BOD. COD samples that were analyzed were matched with a corresponding BOD sample. This allowed for the determination of a correlation coefficient between BOD and COD concentrations. For primary samples the correlation coefficient between COD and BOD was 0.73 and for wetland samples the correlation coefficient was 0.13 meaning that by multiplying primary COD concentration by 0.73 and the wetland COD concentration by 0.13 provides an estimate for the concentration of BOD for the respective sample. This process was conducted and generated the following box plot for the autumn BOD.

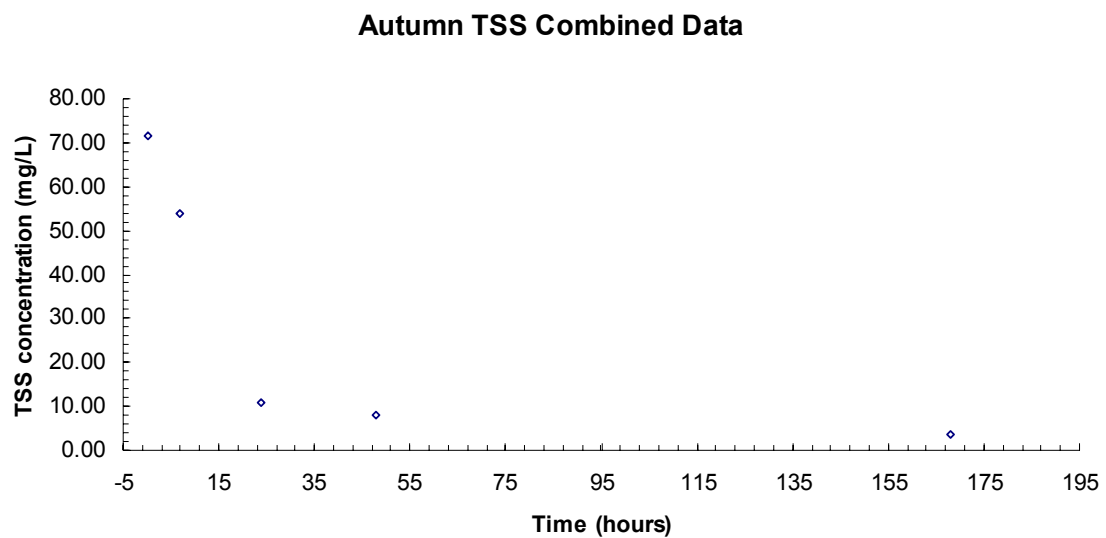


**Figure 35. Box plot of Autumn BOD data as determined from COD concentrations.**

From this box plot the range of BOD values does not vary within the primary effluent nor within the wetland at the various time intervals. BOD therefore is one of the most predictable and treatable pollution parameters within a wetland treatment system.

### 7.1.3 Total Suspended Solids

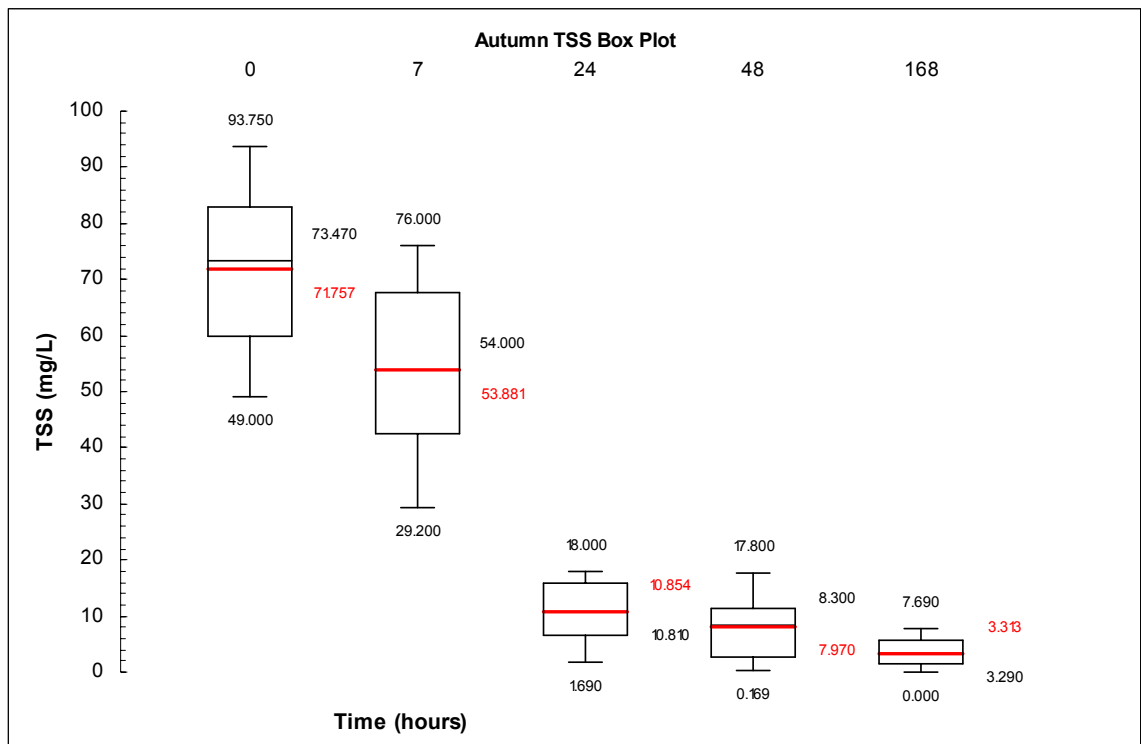
As with temperature, COD and BOD, total suspended solids (TSS) was measured, and data segregated by temperature for the autumn season. The averaged TSS concentration with respect to time is shown in the plot below. The plot demonstrates a rapid drop in TSS concentration in the early stages of treatment followed by performance stability throughout the balance of the treatment cycle.



**Figure 36. Average wetland TSS concentration reduction for autumn season.**



Below is the box plot with all the data for the autumn TSS treatment.



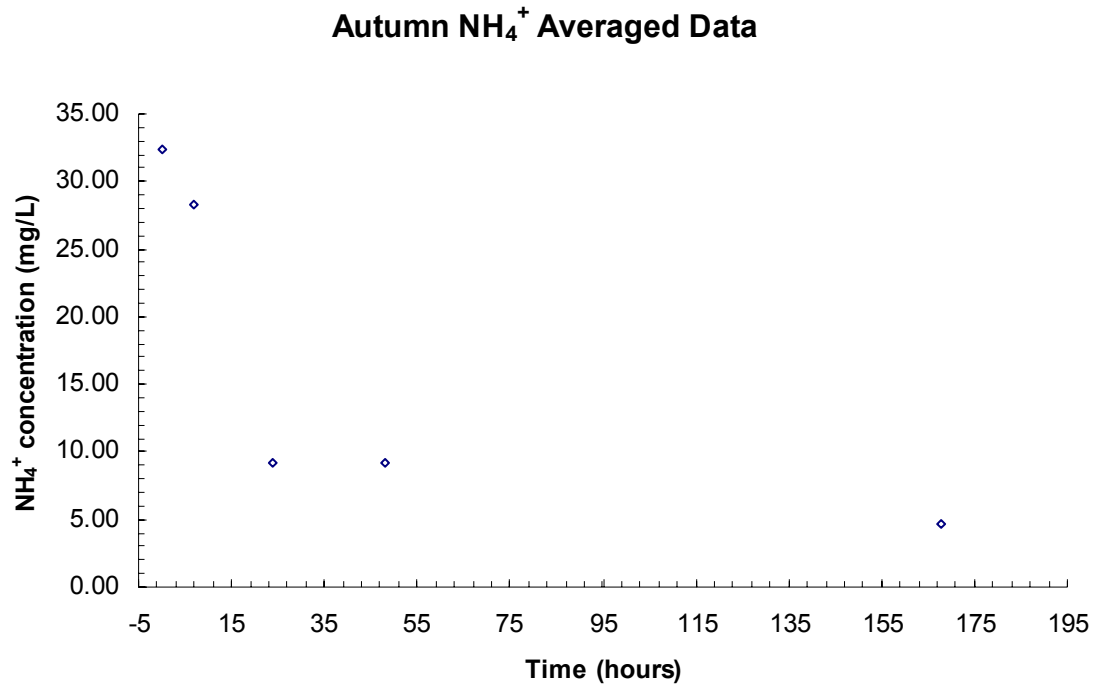
**Figure 37. Box plot of Autumn TSS concentrations.** The red line is the mean and the black line in each box is the median.

What is understood from this TSS box plot is that early in the treatment cycle there exists a wide range of variability in the concentration of TSS. As the treatment cycle progresses, the variability in the TSS concentration reduces and 50% of the data is concentrated around a narrow range of values. Some variability remains as noted by the whiskers, however during the later stages of treatment the concentrations of TSS measured are confined at approximately 3.5 mg/L.

#### 7.1.4 Ammonia as Ammonium Ion ( $\text{NH}_4^+$ )

A total of thirteen experiments were conducted during the autumn season assessing the ammonia concentration reduction in the constructed wetland over the 168

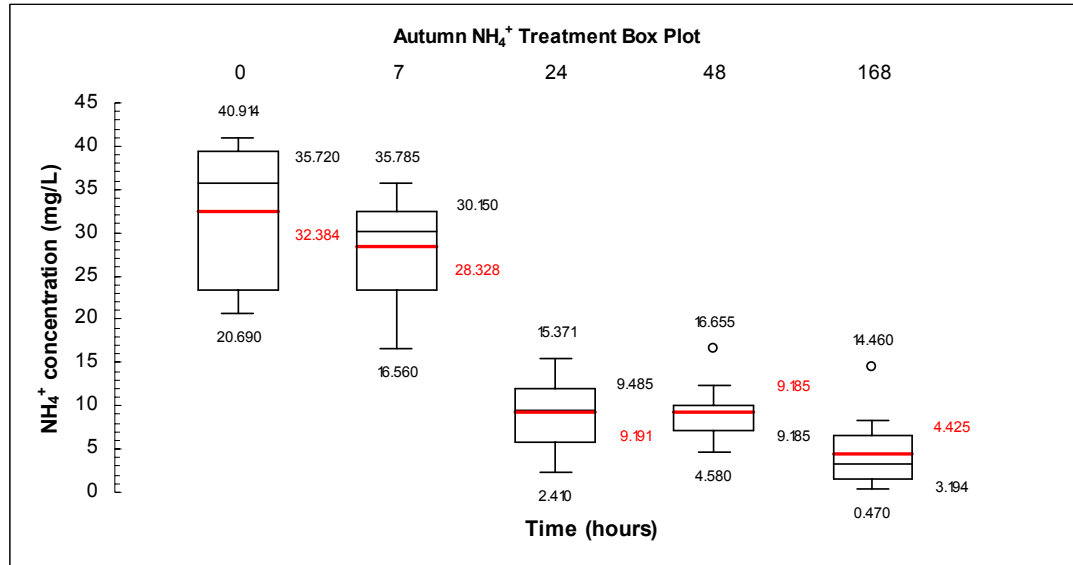
hour retention time. Below is a plot of all the averaged ammonium ion data with respect to time for the autumn treatment period.



**Figure 38. Average wetland  $\text{NH}_4^+$  concentration for Autumn.**

Overall, this plot demonstrates the initial reduction in  $\text{NH}_4^+$  concentration within the first 24 to 48 hours followed by additional treatment over the remaining treatment time. During the autumn an overall 87% reduction in the concentration of  $\text{NH}_4^+$  was determined.

In the following box plot, which includes all the data from the thirteen  $\text{NH}_4^+$  experiments one can see the overall trend in the treatment of ammonia in the system over time.



**Figure 39. Box plot of Autumn  $\text{NH}_4^+$ .**

From this plot one may notice that the  $\text{NH}_4^+$  concentration reduces with respect to time.

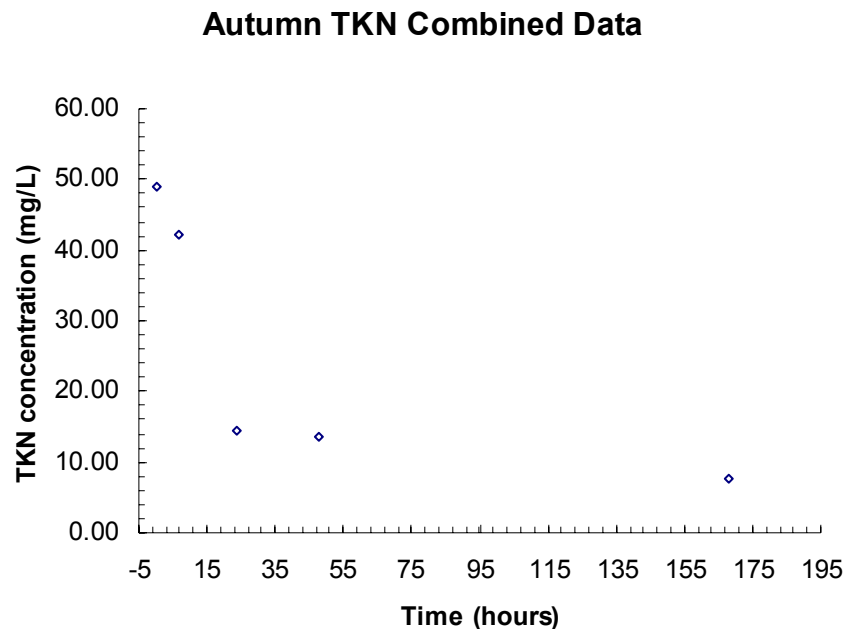
In addition, there is a wider range of concentrations in the early stages of the treatment process and as the treatment process progresses less variability in the data is found.

Noting that there exists less of a range between the maximum and minimum values in the later stages of the treatment process suggests that as the treatment time extends beyond 24 hours the predictability of the effluent concentration of  $\text{NH}_4^+$  is higher. This is important to design features as it supports the need for a residence time in excess of 48 hours to ensure that  $\text{NH}_4^+$  treatment performance has been achieved. However, one can note the existence of two outliers of 16.65 mg/L and 14.46 mg/L at the respective 48 and 168 hour time intervals. These outliers were collected in the later months of the autumn season on dates of November 6, 2003 and November 11, 2003, respectively. These late autumn season samples and the resulting lack of treatment of  $\text{NH}_4^+$  in the treatment cycles that generated these two data points, suggest that the wetland system is transitioning from autumn treatment characteristics toward winter treatment

characteristics. The corresponding water temperatures were found to be 1.8°C and 6.7°C. The temperatures are on the lower end of the optimum temperature range for the treatment of  $\text{NH}_4^+$  in a constructed wetland system. In summary, these data suggest favorable treatment of  $\text{NH}_4^+$  in the autumn season with final concentrations well below the current permit limits.

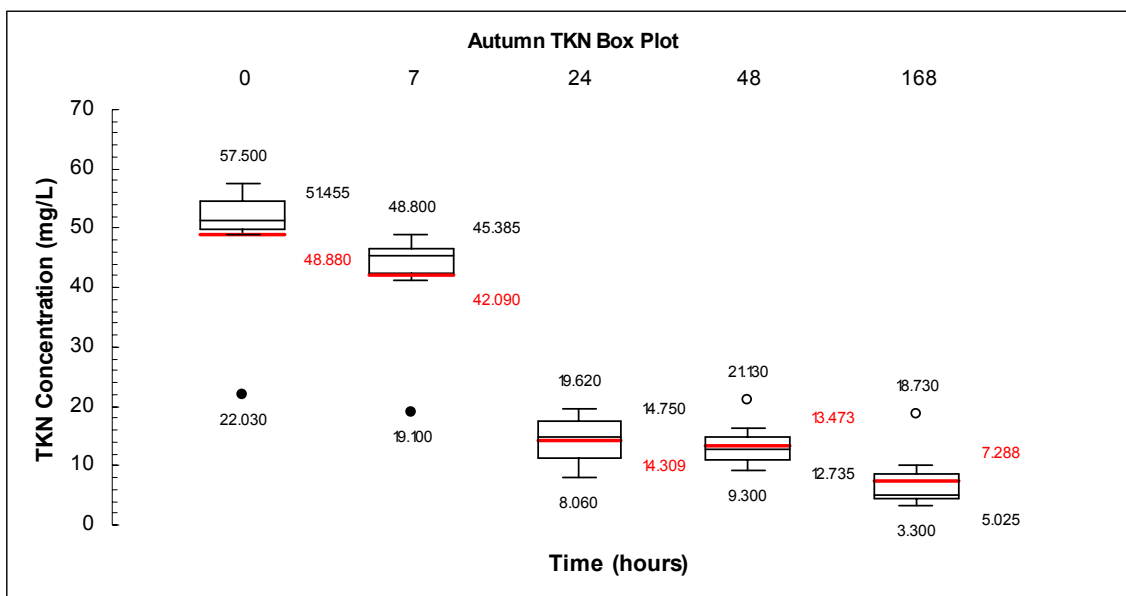
### 7.1.5 Total Kjeldahl Nitrogen

Unlike the other parameters previously discussed total kjeldahl nitrogen was investigated only in the fall of 2003 with eight total experiments. The plot below is the combined averages of TKN concentration at the sample times. With this plot, we can see that TKN treatment occurs within the first 24 – 48 hours of each treatment cycle.



**Figure 40. Average wetland TKN concentration reduction for autumn season.** The data points represent the average TKN concentration at each particular sampling time.

The following box plot shows all the data for the TKN presented in one chart.



**Figure 41. Box plot of autumn TKN.**

Again, these data demonstrate a decrease in the concentration of TKN with respect to time. Also of interest as compared to the other parameters is the lack of variability even in the early stages of TKN treatment. The range of TKN concentration values are much narrower than with the other pollutants investigated. Consistent with the other pollutants is that after 24 hours the bulk of the treatment has been conducted and we find the characteristic drop in nutrient concentration. More outliers are found with TKN than with any of the other pollutants suggesting that the potential for variable concentrations at any given time is high. The two elevated levels at the 48 and 168 hour times were taken late in the season and are consistent with the high levels of  $\text{NH}_4^+$  determined for the same experiment and discussed in the previous section.

### 7.1.6 Fall Summary

The following table provides average data for the fall experiments. The bottom row is the percent reduction (as “% Red”) in the concentration over the treatment time in the wetland. Time zero (0) represents the primary effluent being loaded into the wetland.

| Time  | Temp | pH    | COD | TSS   | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> /NO <sub>2</sub> | TDS | Salinity | Conductivity | TKN   | BOD    |
|-------|------|-------|-----|-------|------------------------------|----------------------------------|-----|----------|--------------|-------|--------|
| 0     | 18.0 | 7.403 | 306 | 71.76 | 32.38                        | 0.211                            | 594 | 0.6      | 1150         | 48.88 | 176.38 |
| 7     | 15.3 | 7.320 | 243 | 53.88 | 28.33                        | 0.061                            | 590 | 0.6      | 1089         | 42.09 |        |
| 24    | 10.2 | 7.191 | 70  | 10.85 | 9.19                         | 0.060                            | 691 | 0.7      | 2355         | 14.31 |        |
| 48    | 9.3  | 7.206 | 72  | 7.97  | 9.18                         | 0.085                            | 596 | 0.6      | 1137         | 13.47 |        |
| 168   | 8.4  | 7.150 | 51  | 3.59  | 4.70                         | 0.625                            | 598 | 0.6      | 1143         | 7.62  | 4.60   |
| % Red | 53%  | 3%    | 83% | 95%   | 85%                          | -196%                            | -1% | 3%       | 1%           | 84%   | 97%    |

**Table 21. Summary of autumn season wetland treatment performance.** Time is in hours, concentration units are mg/L and the last row is the overall percent reduction.

These data in the table 21 reveal a slight increase in the concentration of nitrate/nitrite nitrogen, with stable pH, total dissolved solids (TDS), salinity and conductivity over the course of the treatment. The increase in nitrate/nitrite is attributed to ammonia that has nitrified with a portion of the nitrate produced not undergoing denitrification. BOD was only taken at the beginning and end of each batch treatment experiment. Here, as stated previously, the average BOD concentration has an overall reduction of 97% during the fall season.

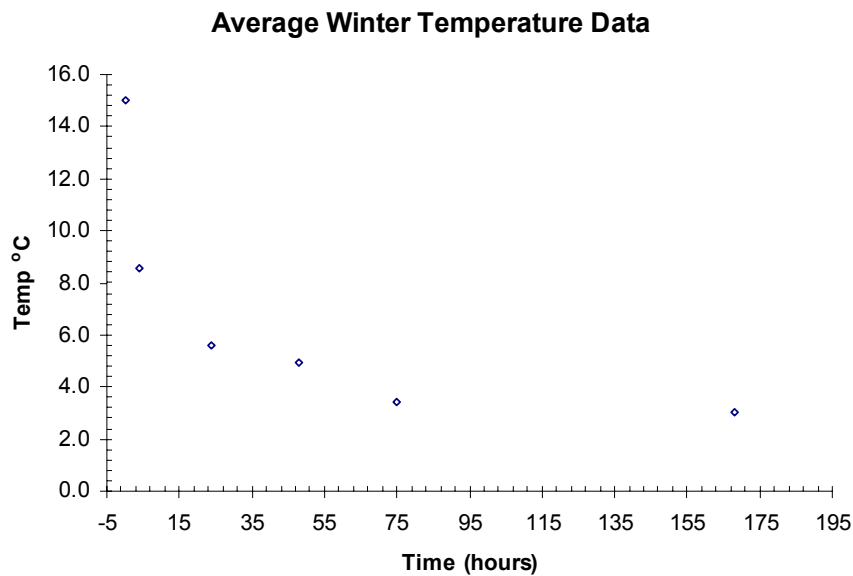
In summary, the fall season provides good conditions for the treatment of criteria pollutants. The mild weather allows the wetland to operate without the stress of the summer heat or the chill of the winter cold. Each of the criteria pollutants, on the average, fell below the discharge permit concentration, however total nitrogen (TN) is 12.32 mg/L, determined by adding the concentration of NH<sub>4</sub><sup>+</sup> and TKN together, is slightly above the targeted VNRP 30 day average of 10 mg/L.

## 7.2.0 Winter

Seventeen experiments were conducted under winter time operating conditions between 2002 and 2004. Shown below, in the following sections are plots and charts that provide an understanding of what the behavior was for each specific physical or chemical parameter. During the winter time a 5-10 cm layer of ice formed on the experimental wetland system and holes were drilled through this ice layer to remove spatially variable samples.

### 7.2.1 Temperature

Below is a representative plot of how the water temperature of the experimental constructed wetland system changed with respect to time during winter time operations.

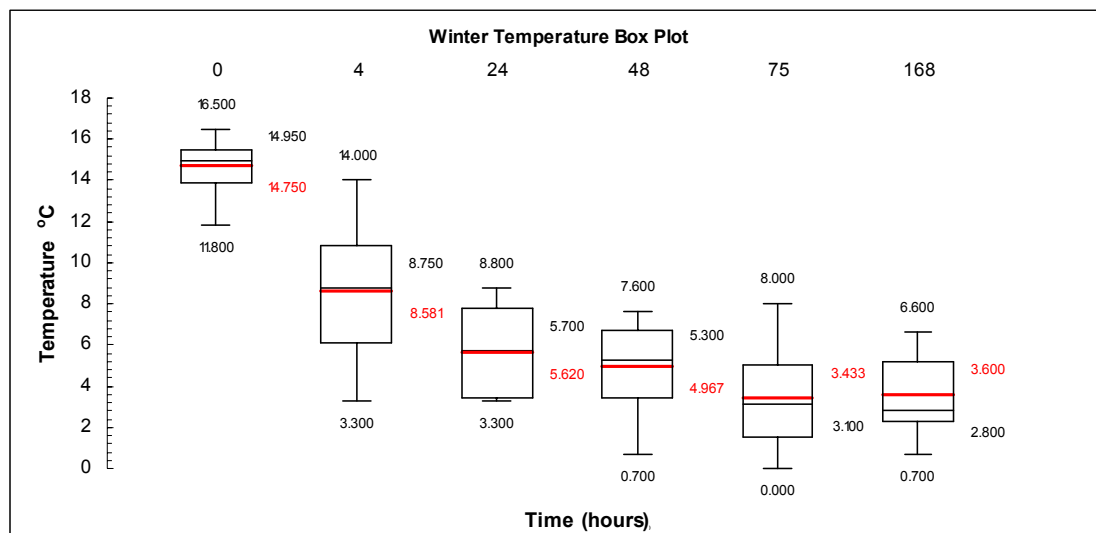


**Figure 42. Average wetland temperature reduction for winter season.**

This plot represents what was found during the winter time with respect to temperature change. The initial data point is the temperature of the primary effluent that enters the experimental treatment system. As time progresses the temperature of the wetland water

drops. Of particular note is that the temperature did not drop to freezing but, on the average, remained between 2 and 4°C. Also, as these data suggest, there is a rapid decrease in temperature within the first 30 to 50 hours of treatment and overall stabilization of the temperature to just above freezing thereafter.

Below is the box plot for winter time temperature measurements at selected time intervals.



**Figure 43. Box plot of winter temperature data from 0 to 168 hours of treatment.**

With the box plot, temperature variability is present in the early stages of treatment. This is suspected to be primarily due to different mixing levels of primary effluent in Cell 1. Even during the wintertime temperatures after 168 hours were in one case as high as 6.6°C, however, 50% of the temperature measurements fell between 2°C and 4°C at the 168 hour sample time.

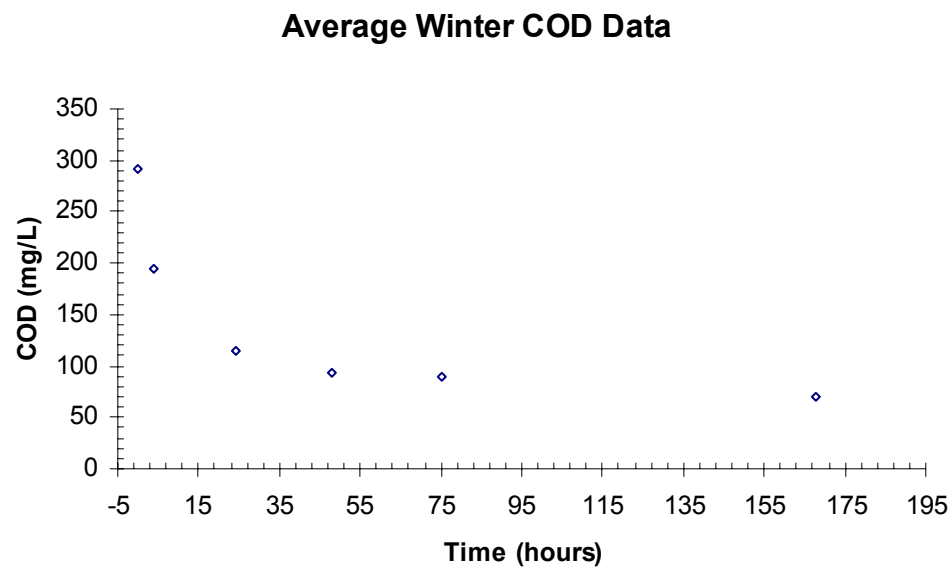
As discussed before, during the winter time an ice layer formed on the surface of the wetland treatment system. This ice and resulting accumulation of snow provided modest insulation from the atmospheric conditions over the course of the 168 hour



treatment cycles. This enabled the temperature to remain just above freezing and allowed wastewater to cycle through the wetland system below the layer of ice.

### 7.2.2 COD and BOD

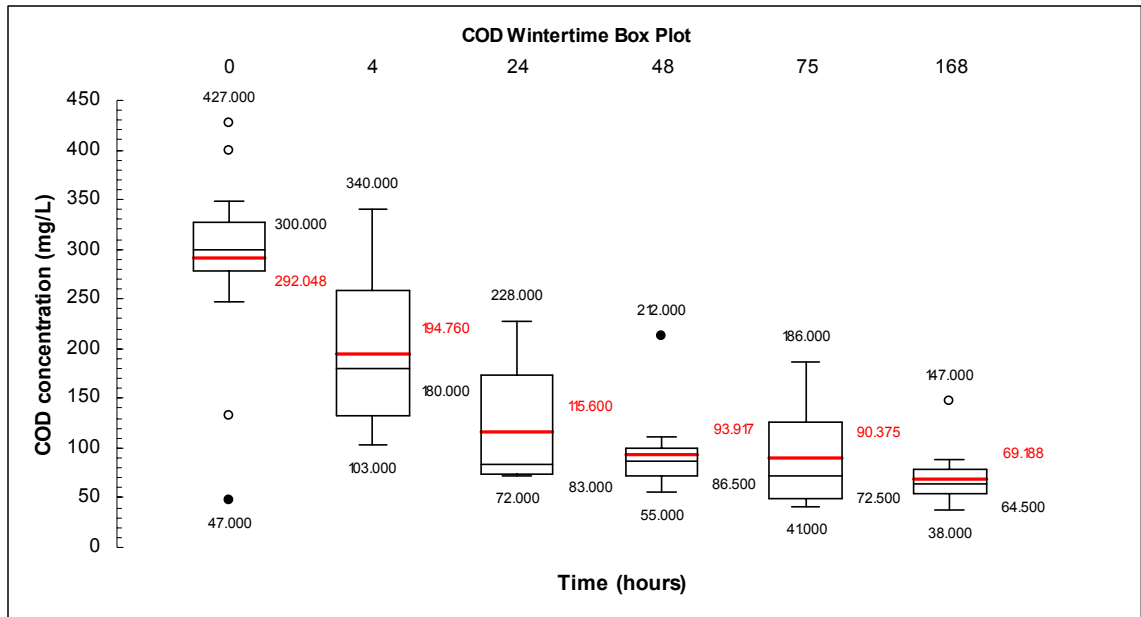
Below is a representative plot of the average COD concentration with respect to each of the winter sample times.



**Figure 44. Average wetland COD reduction for winter season.**

Overall, a more gradual drop in the concentration of COD in the early stages of treatment during the winter time is found as compared to the fall. In addition, after approximately 48 hours, no additional treatment of COD is realized.

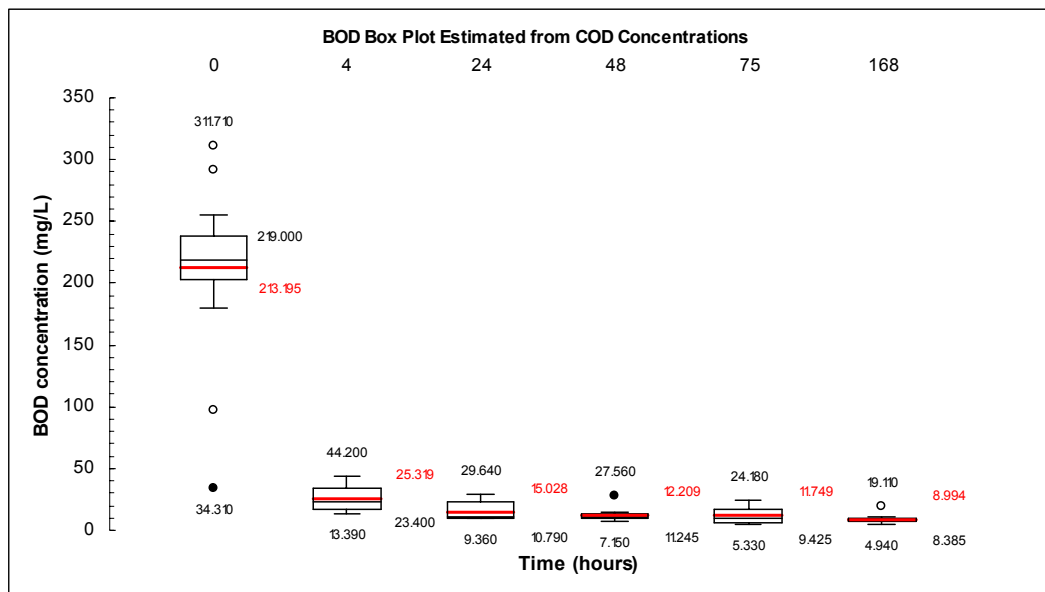
A box plot of all the data is shown below.



**Figure 45. Box plot of winter COD data.**

This box plot illustrates the wide variability in COD concentrations at any particular time within the wetland over the course of the treatment cycle during the winter months. We have outliers that can skew the data set one direction or the other. These outliers can impact both design equations and regulatory compliance. However, 50% of the data is concentrated around reasonable values at both the 48 and 168 hour sample times lending some credibility to the ability for wetland systems to handle COD during the wintertime.

Below is a box plot of BOD data generated from the COD data.

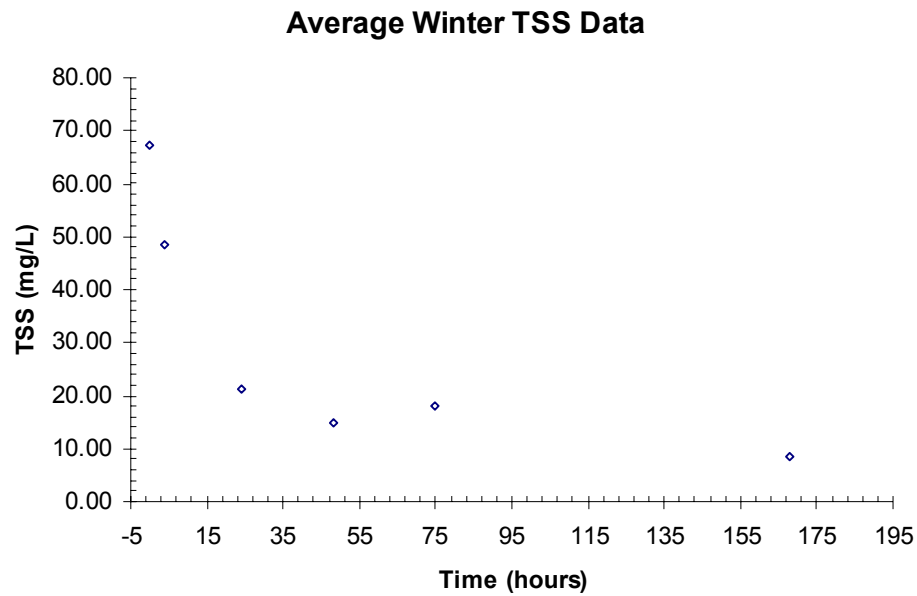


**Figure 46. Box plot of winter BOD data generated from COD values.**

These BOD values were calculated from COD values using the correlation coefficients discussed in the autumn section. As expected and similar to COD wide variability is found within the primary effluent being introduced with concentration stability and predictability in the later stages of the treatment cycle with winter time operating conditions.

### 7.2.3 Winter TSS

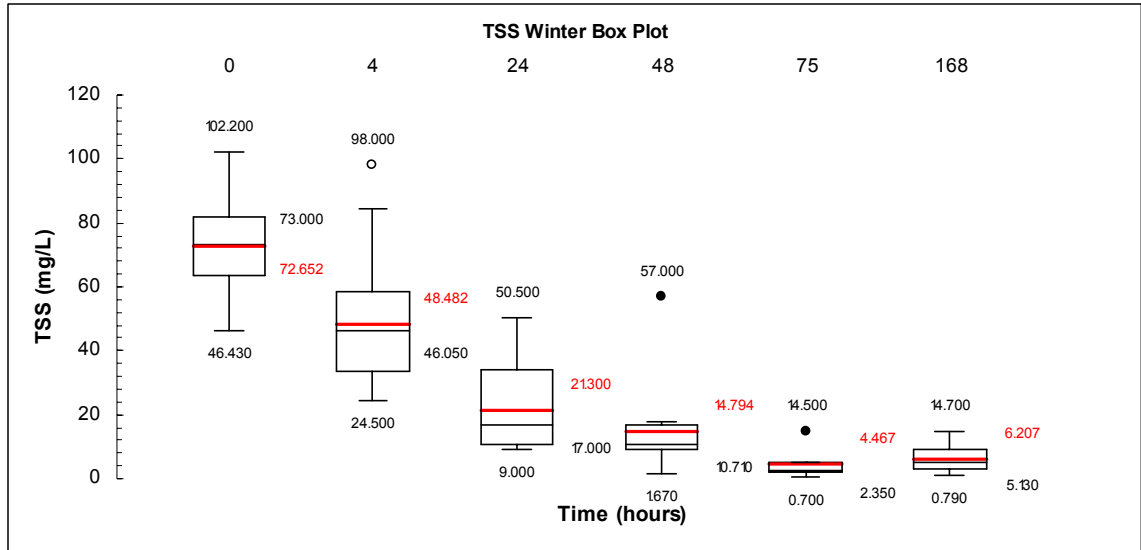
Total suspended solids is the next parameter that is discussed.



**Figure 47. Average wetland TSS reduction for winter season.**

These TSS data are very similar to the corresponding COD data plotted above, in that the drop in the TSS concentration is more gradual within the first 24 to 48 hours as compared to the autumn season. Again, these data plotted show stable TSS concentrations after approximately 48 hours of treatment with very little change in concentration thereafter.

A box plot of the wintertime TSS data is shown below.



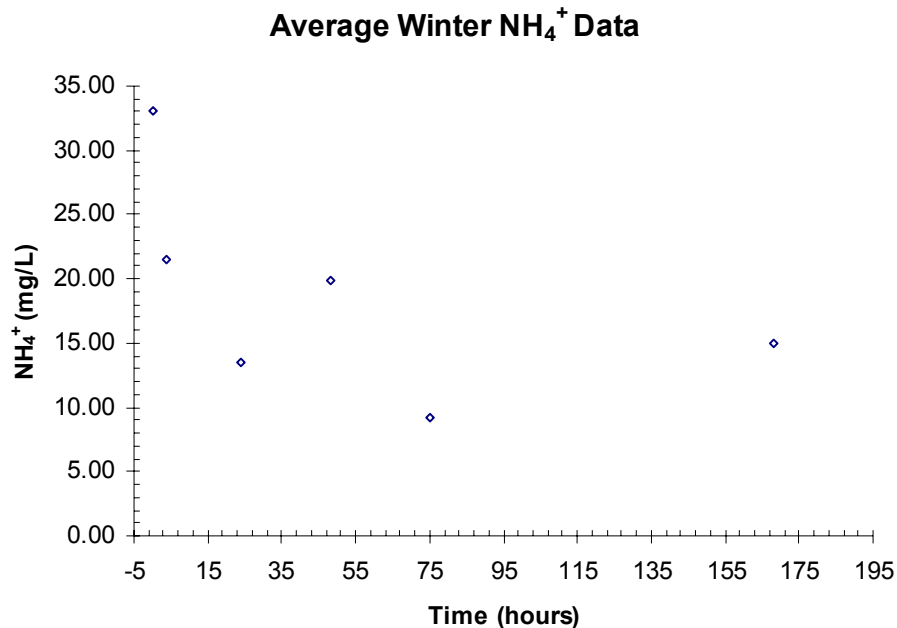
**Figure 48. Box plot of winter TSS data.**

These data presented in figure 48 demonstrate a wide range of TSS values within the first 24 hours of treatment. However, as the treatment progresses we find that the data settles down and the range of values contracts. Outliers are present during the 4, 48, and 75 hour sample time however, the final sample event at 168 hours provides a predictable range of values. However, note that the high end of the range exceeds the permit limits for TSS. Overall, these data demonstrate a gradual reduction in the concentration of the TSS with respect to time during winter time treatment conditions.

#### 7.2.4 Ammonia as $\text{NH}_4^+$

The next pollutant analyzed for winter time performance is  $\text{NH}_4^+$ . Approximately 50% of the influent N is found in the form of  $\text{NH}_4^+$ . Therefore the ability to reduce this form of nitrogen is very important as  $\text{NH}_4^+$  contributes to the total nitrogen content within the effluent. Total nitrogen (TN) is the metric used within the discharge permits and the ability to stay within permit limits for TN during the wintertime is important to both

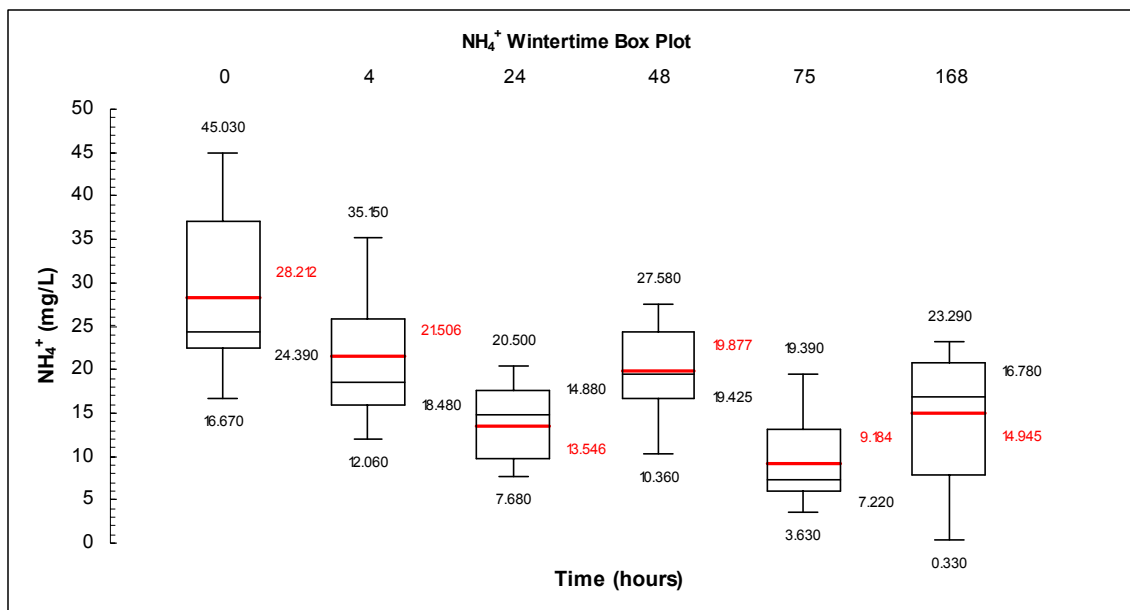
municipalities and their regulatory agencies. Below we have a plot of the average concentration of  $\text{NH}_4^+$  with respect to time.



**Figure 49. Average wetland  $\text{NH}_4^+$  reduction for winter season.**

These data demonstrate the challenges faced with the treatment of  $\text{NH}_4^+$  during the winter months. A drop on the concentration  $\text{NH}_4^+$  is found however, not to the extent that support permit conditions required for effluent discharge. These data demonstrate the reality faced with a reduction in the temperature of the wetland that limits the microbial degradation of  $\text{NH}_4^+$ . This plot is indicative of the wide range of variability and lack of predictability of treatment performance for  $\text{NH}_4^+$  under winter time conditions.

In summary,  $\text{NH}_4^+$  was reduced by 56% under wintertime conditions. The data for  $\text{NH}_4^+$  is provided in the box plot below.

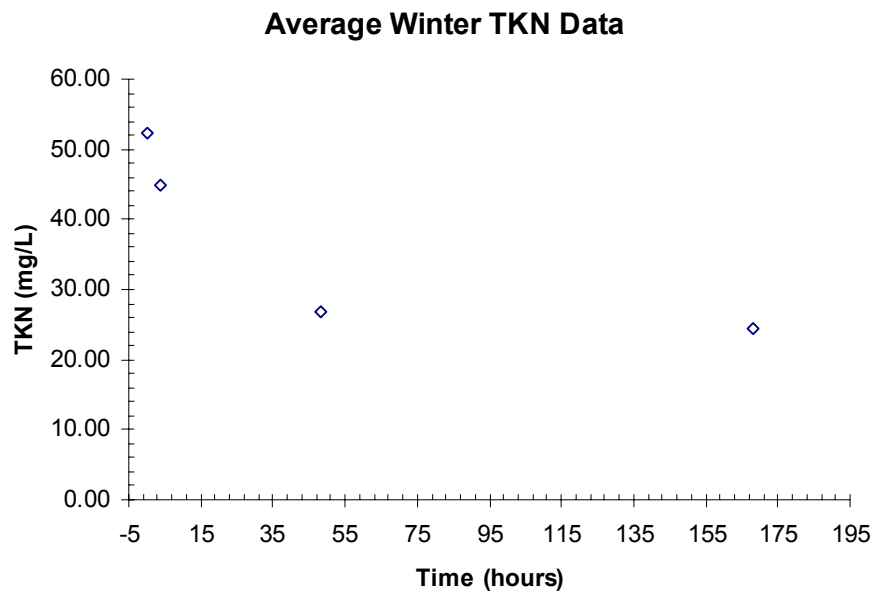


**Figure 50. Box plot of winter  $\text{NH}_4^+$  data.**

These data presented in the box plot suggest that there exists a wide range of values for ammonium ion concentration at any particular time during the course of the treatment cycle during the winter time. No outliers are found and a gradual drop in the concentration of the  $\text{NH}_4^+$  with respect to time is demonstrated however, 50% of the data at the 168 hour exceeds the 10 mg/L total nitrogen permit requirement thus presenting challenges from a regulatory perspective.

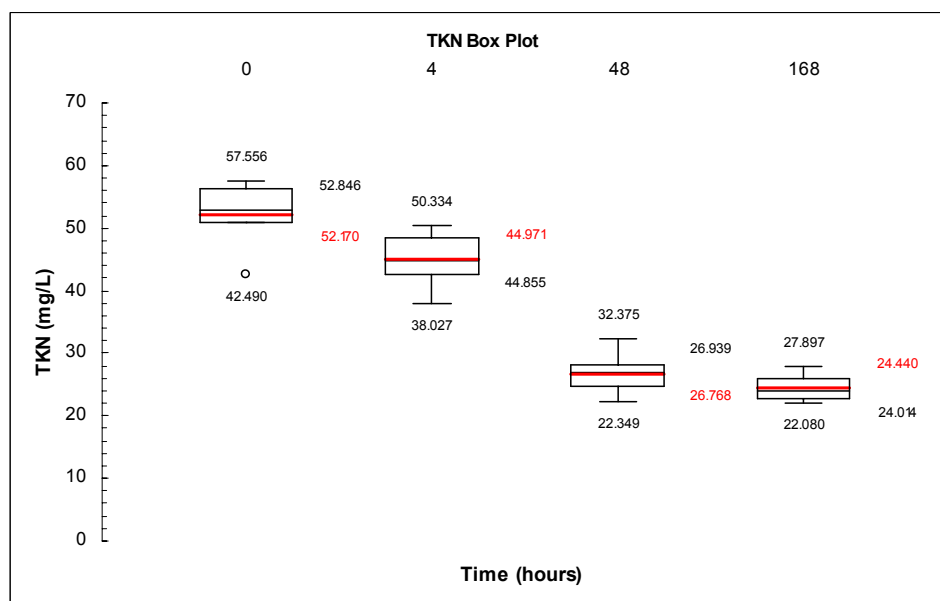
### 7.2.5 Wintertime TKN

The next parameter discussed is Total Kjeldahl Nitrogen or TKN. TKN is important as it represents the biological nitrogen present in the wastewater such as proteins and amino acids. TKN is the other form of nitrogen that provides a significant contribution to regulated TN discharge concentration. The following plot shows the average of all the TKN concentrations plotted with respect to time.



**Figure 51. Average wetland TKN reduction for winter season.**

A gradual decrease in the concentration of TKN is realized within the first 24 to 48 hours with the characteristic stabilization and no treatment occurring after approximately 75 hours. The overall reduction in TKN concentration during the wintertime was 50% however, this was not enough to reduce the TN concentration below the 10 mg/L permit requirements. Below one may see the box plot of all the TKN data.





**Figure 52. Box plot of winter TKN data.**

As the box plot demonstrates, for each of the sample times 50% of these data are concentrated around specific values. This suggests that the concentration of TKN at the end of the treatment cycle at any particular time throughout the treatment cycle can be predicted with a relative amount of assurance that the actual value will be close to the predicted value. However, there is a significant lack of treatment performance as only a 50% reduction in the concentration of TKN is realized and the combined TN concentration, as stated previously, is well above the permit limit.

### **7.2.6 Wintertime Conclusions**

Wintertime presents significant challenges all related to the cold temperatures. The treatment of COD, BOD and TSS is quite good during the wintertime however, the microbial mediated treatment of  $\text{NH}_4^+$  and TKN is challenged by the colder temperatures found in the wetland during the wintertime. COD, BOD and TSS are generally mechanical treatment operations with the treatment potential related to the rate of settling of suspended solids and other suspended degradable particulates. The reduction in the rate of treatment for COD, BOD and TSS during the wintertime was attributed to viscosity changes found in the cooler water. The wetland was operational even during the coldest days of winter as there was a layer of ice and snow that provided a certain level of protection from the ambient air temperature and prevented a complete freeze up of the system. Below is a chart of the average data collected under wintertime operating conditions.

| Time  | Temp | pH    | COD | TSS   | NH4   | NO3/NO2 | TDS | Salinity | conductivity | TKN   | BOD    |
|-------|------|-------|-----|-------|-------|---------|-----|----------|--------------|-------|--------|
| 0     | 15.0 | 7.438 | 292 | 67.29 | 33.11 | 0.254   | 641 | 0.6      | 1246         | 52.17 | 157.23 |
| 4     | 8.6  | 7.400 | 195 | 48.48 | 21.51 | 0.259   | 615 | 0.6      | 1196         | 44.97 |        |
| 24    | 5.6  | 7.208 | 116 | 21.30 | 13.55 | 0.020   | 465 | 0.5      | 931          |       |        |
| 48    | 5.0  | 7.156 | 94  | 14.79 | 19.88 | 0.014   | 549 | 0.5      | 1049         | 26.77 |        |
| 75    | 3.4  | 7.277 | 90  | 18.02 | 9.18  | 0.309   | 535 | 0.5      | 1063         |       |        |
| 168   | 3.0  | 7.216 | 69  | 8.63  | 14.95 | 0.142   | 548 | 0.5      | 1054         | 24.44 | 8.30   |
| % Red | 80%  | 3%    | 76% | 87%   | 55%   | 44%     | 14% | 18%      | 15%          | 53%   | 95%    |

**Table 22. Summary of winter season wetland treatment performance.**

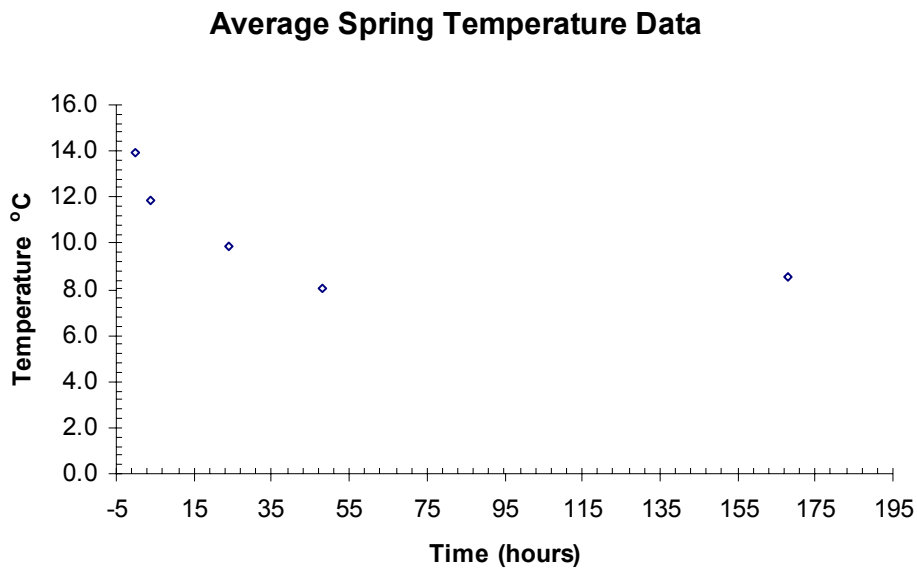
As these data suggest, nitrate and nitrite concentrations provide and insignificant contribution to the overall TN concentration. From this table one may note little change in the pH, TDS, salinity and conductivity of the wetland water. These data suggest that COD, BOD and TSS are still treated effectively during the winter time but TN treatment is not sufficient to meet permit requirements.

### **7.3.0 Spring**

The data set under spring time conditions is the smallest of all the seasons and is limited to the spring of 2003 and the spring of 2004. Six experiments were conducted during the spring of 2003 and two experiments were conducted in the spring of 2004. Construction of the Biological Nutrient Removal (BNR) process at the City of Missoula wastewater treatment plant halted the collection of data in the spring of 2004. This relatively limited data set however did provide some interesting results which are discussed below.

#### **7.3.1 Temperature**

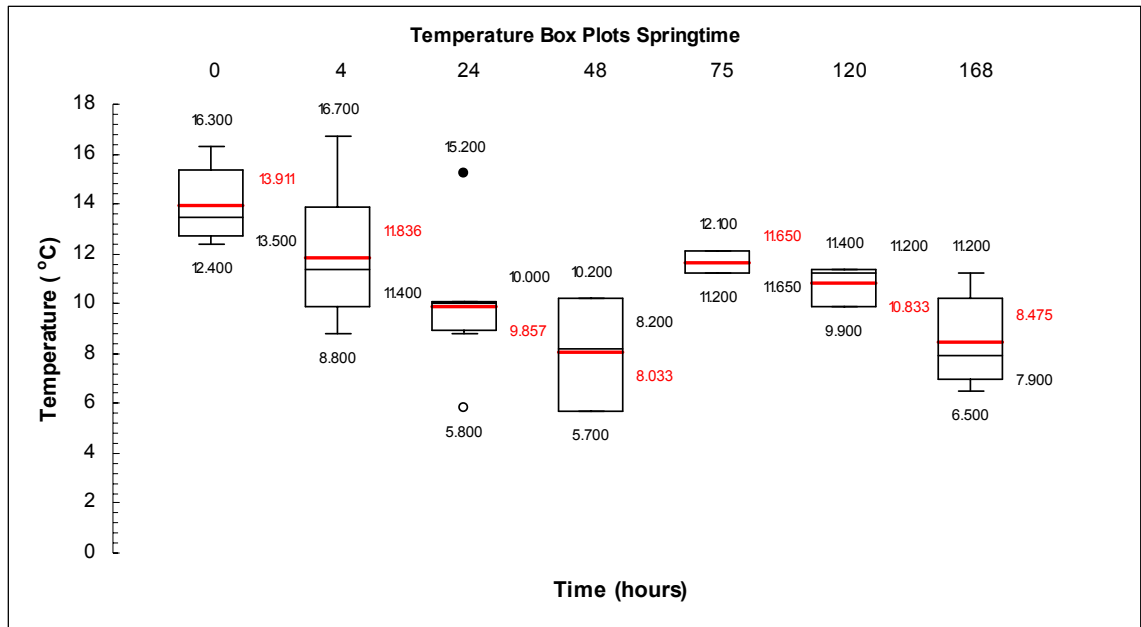
The temperature of the wetland during the spring time was affected by cold nights with increasingly warm days. Below is a representative plot of the average temperature reduction within the wetland with respect to time during the springtime operating conditions.



**Figure 53. Average wetland temperature reduction for spring season.**

The above plot reveals a drop in temperature experienced during the first 24 to 48 hours of treatment followed by a stabilized temperature within the wetland for the remainder of the treatment cycle. The temperature range of the wetland, under springtime conditions and after 48 hours of treatment varied between 12°C and 6°C and the average temperature of the wetland water then increased over the course of the treatment time.

Below is a box plot with all of the temperature data for the springtime experiments.

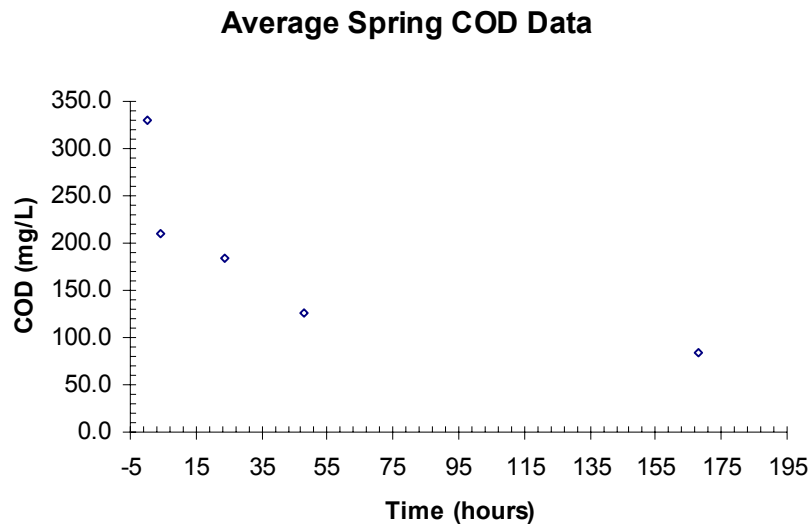


**Figure 54. Box plot of winter temperature data.**

These data presented in the box plot suggest that under spring time operating conditions the wetland water temperature varies over the course of the treatment cycle. The initial temperatures at the zero hour are dominated by the temperature of the primary effluent being introduced into the wetland system. As the treatment cycle progresses the ambient air temperature beings to have a larger level of influence over the wetland water temperature. From this plot one may note some outliers as would be expected in a natural system, however, as treatment progresses and wetland water is influenced by the ambient air temperature the wetland temperature variability is reduce.

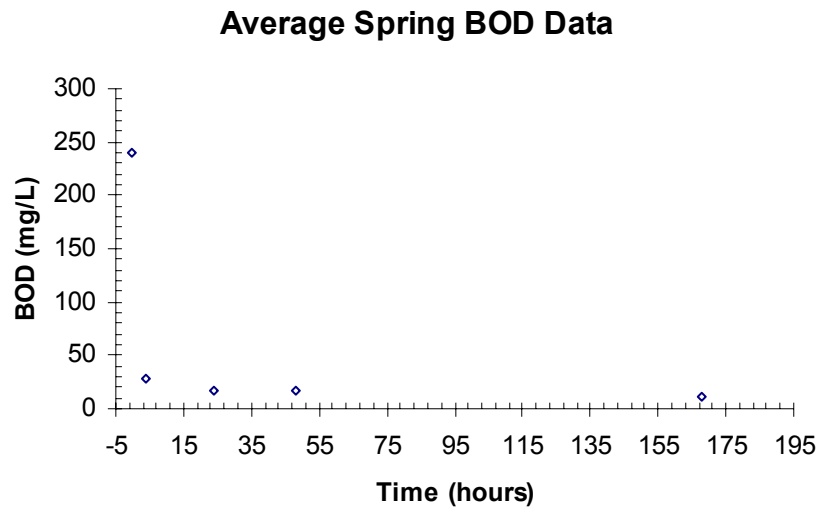
### 7.3.2 COD and BOD

It is instructive to review the data for the reduction in COD and BOD with respect to time during springtime operating conditions keeping in mind the same plots from the autumn data.



**Figure 55. Average wetland COD reduction for spring season.**

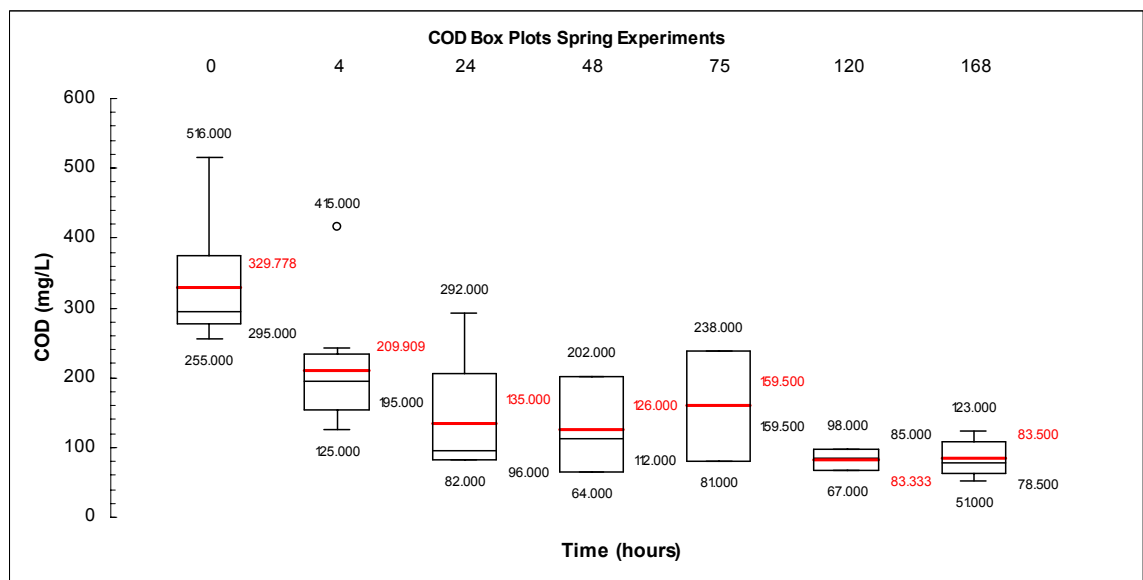
Recalling the plots from the autumn data and in comparison to winter time COD concentration reduction with respect to time, again the familiar trend, as compared to the autumn data, is evident in that the COD concentration drops very quickly within the first 24 to 48 hours and settles out to a minimum value soon thereafter. By averaging all the COD data and combining into one plot one may notice that early stage treatment is less rapid as compared to autumn conditions but more rapid as compared to wintertime conditions. Of note is that an acceptable reduction in COD concentration is achieved during spring time conditions after ~95 hours of treatment. By taking the COD data, BOD data was generated. Below is a plot of that BOD data as generated from COD.



**Figure 56. Average wetland BOD reduction for spring season calculated from COD data.**

As expected, a rapid drop in BOD is realized as particulates and other suspended solids settle within the first few hours of treatment. This is followed by stabilized BOD concentrations throughout the remainder of the 168 hour treatment cycle.

The box plot for springtime COD data as shown below.

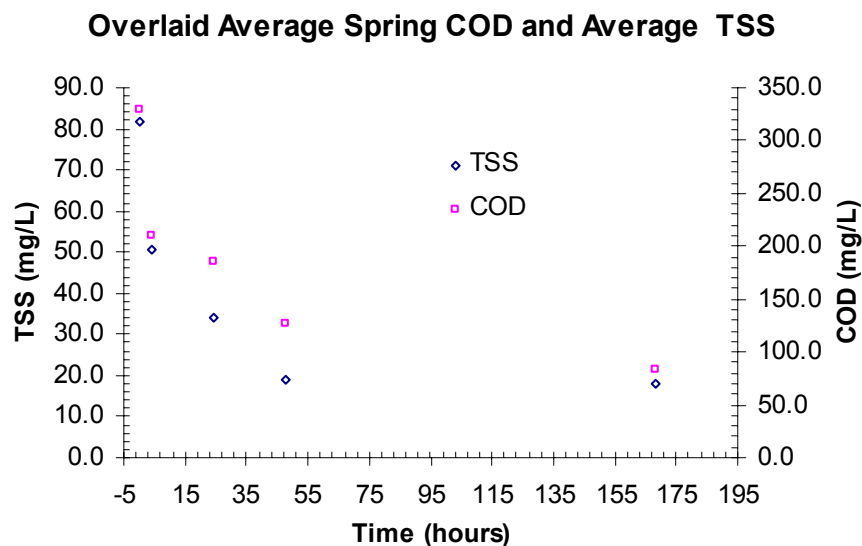


**Figure 57. Box plot of spring COD data.**

These data presented in the box plot suggest a wide range of variability in the zero hour sampling which is highly influenced by the primary influent being introduced to the wetland and the variability found with the COD concentrations in the primary effluent. As the treatment progresses these data demonstrate a drop in the concentration of COD with less variability in the data towards the end of the treatment cycle with 50% of the data concentrated between 62 mg/L COD and 102 mg/L COD.

### 7.3.3 TSS

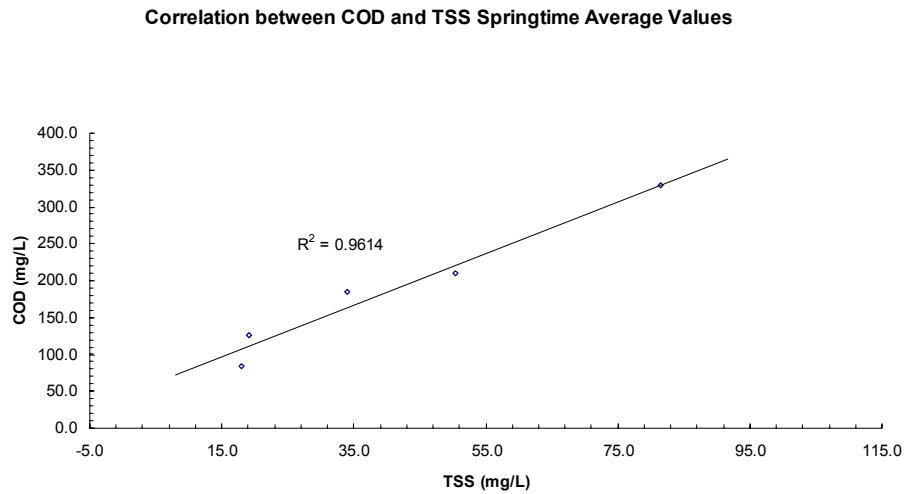
The next parameter evaluated is springtime total suspended solids (TSS). Below is a plot of the average TSS values overlaid against the average COD values at each particular time plotted with respect to time.



**Figure 58. Overlaid average wetland COD and TSS values for spring season.**

These data show a decrease in TSS concentration with respect to time with most of the treatment occurring within the first 48 hours with very little change in TSS concentration thereafter. These data plotted suggest a correlation between COD

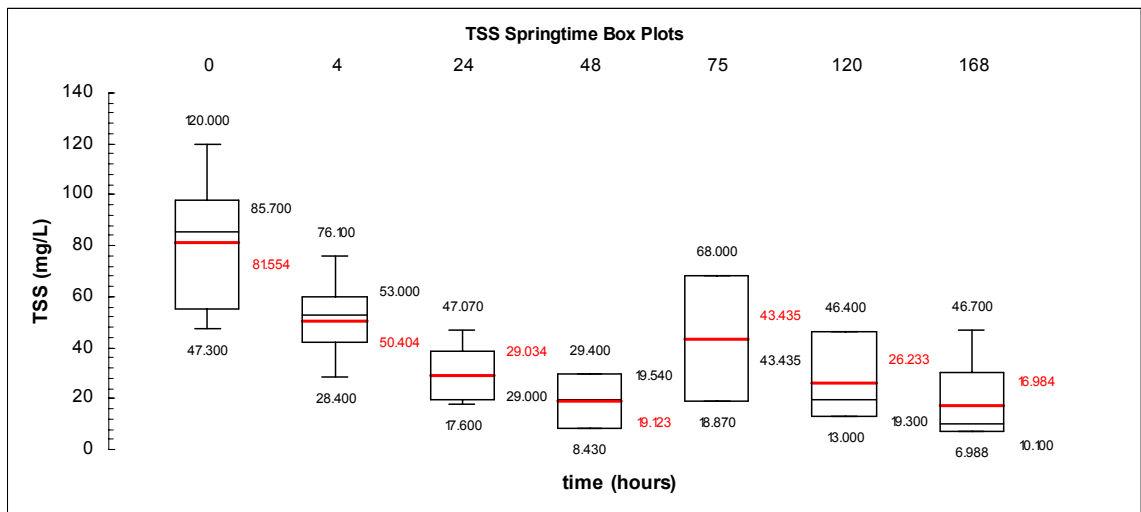
concentration and TSS concentration. This correlation may also be represented by plotting TSS with respect to COD as shown in the plot below.



**Figure 59. Correlation plot between average TSS and COD values for spring season.**

The correlation coefficient approaches unity suggesting a good relationship throughout the treatment cycle between the COD concentration and the TSS concentration.

The variability in the TSS data is demonstrated in the box plot below.



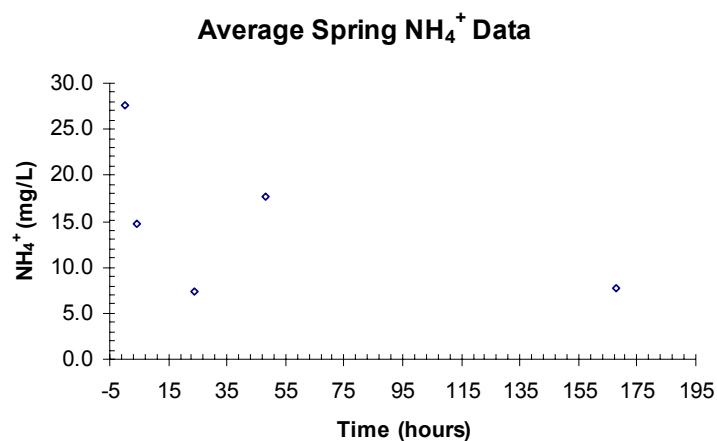
**Figure 60. Box plot of spring TSS data.**



As would be expected, there exists a wide range of TSS concentration values at the zero hour, the concentration of which is dominated by the primary influent. A systematic decrease in the concentration of TSS is realized within the first 48 hours however, a wide range of values present themselves just past the mid-way point through the treatment cycle. At the final sample time of 168 hours one may note that 50% of the data is concentrated around 7 mg/L and 30 mg/L, values that fall below the permit limits. However, in at least one instance at the 168 hour sample time, the TSS value exceeded the permit limit at 46.7 mg/L. It must be noted that the TSS values are highly dependent on sampling technique as disruption of the surface of plants can dislodge particles that are ultimately part of the sample matrix. In addition, any algae or duckweed found in the sample matrix will skew the results.

#### 7.3.4 $\text{NH}_4^+$

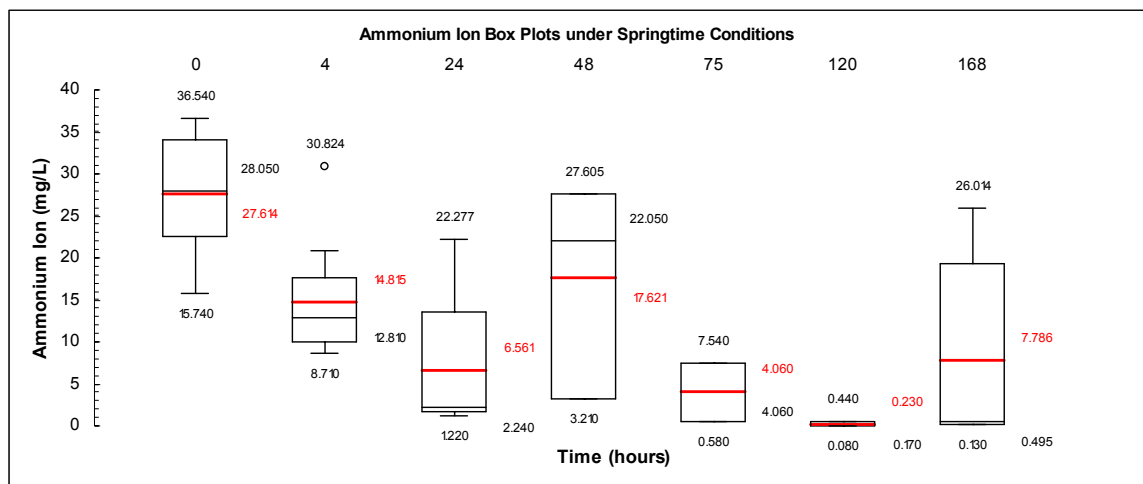
With the warmer conditions found during the spring time the treatment of ammonia as  $\text{NH}_4^+$  is better as compared to wintertime conditions. Below we have a plot of the average ammonium ion concentration data with respect to time.



**Figure 61. Average wetland  $\text{NH}_4^+$  reduction data for spring season.**

As these data suggest, a considerable amount of variability exists during the spring time with respect to ammonium ion concentration. An overall 71% reduction in ammonium ion concentration was found under spring time operating conditions. Removing the data that was borderline wintertime conditions we find a 99% reduction in the concentration of  $\text{NH}_4^+$  with respect to time over the course of the treatment cycle. With this plot we find a rapid decrease in the concentration with respect to time with the bulk of the treatment found in the first 24 to 48 hours.

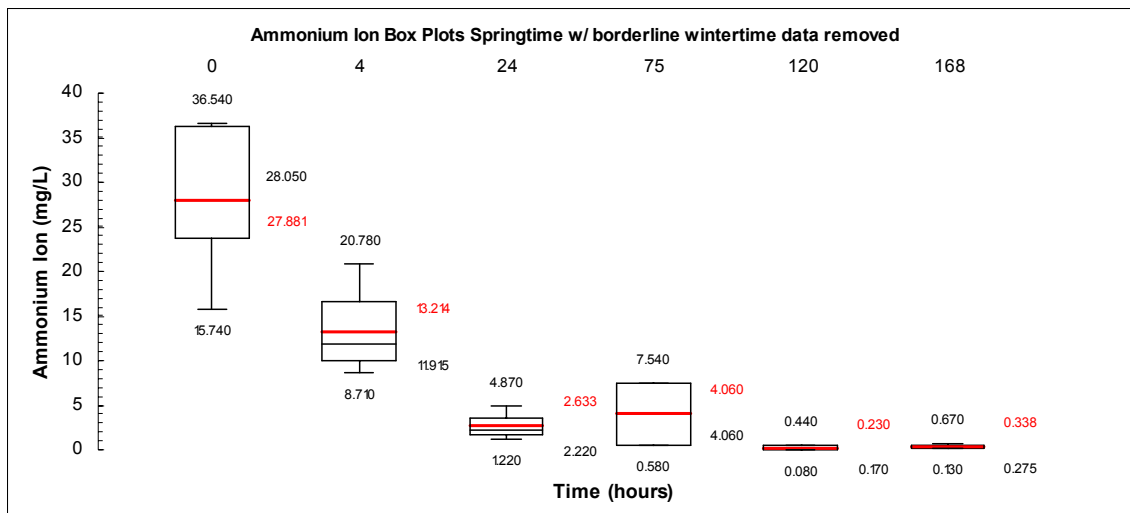
Below we have the ammonium ion box plot for all the springtime ammonium ion concentration data. These data suggest a wide range of variability in ammonium ion concentrations at any particular time in the wetland during springtime operating conditions. The 168 hour data includes data from an experiment conducted in early March of 2003 that provided borderline winter time/spring time temperature conditions.



**Figure 62. Box plot of spring  $\text{NH}_4^+$  data.**

Overall, there is a trending decrease in the concentration of ammonium ion with respect to time however there exists a wide range of concentrations at the 48 hour and the 168

sample time. The box plot below has the questionable and borderline wintertime/springtime data removed.

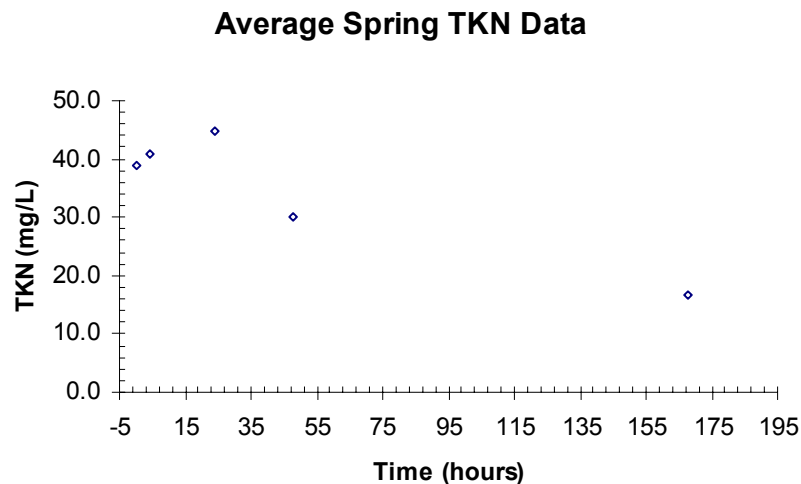


**Figure 63. Box plot of spring  $\text{NH}_4^+$  data with questionable outliers removed.**

With the questionable data removed one may note a decrease in the concentration of ammonium ion within the first 24 hours with very little variation in the data after this time. This consistency from experiment to experiment is evident in these data and this consistency is desirable from an operations management and discharge permit perspective. However, noting the previous box plot there is still the chance during the springtime for cool conditions that will limit the performance of the wetland and potentially lead to a permit violation(s).

### 7.3.5 Total Kjeldahl Nitrogen

Below is a plot of the average TKN reduction with respect to time under springtime operating conditions.



**Figure 64. Average wetland TKN reduction data for spring season.**

Limited TKN data was collected but these data suggest an overall 57% decrease in the concentration of TKN over the course of the treatment cycles under springtime operating conditions. This considers the questionable springtime data highlighted in the previous ammonium ion section. If we remove these questionable spring time data points we find an 86% reduction in the concentration of TKN over the course of the treatment cycle.

### **7.3.6 Springtime Summary**

The springtime is noted for early season cold conditions followed by late season increase in ambient air temperature and sunlight. As expected this contributes to significant variability in the concentrations of pollutants and nutrients investigated. Below is the springtime data set showing the averages at each respective sample time.

| Hrs   | Temp | pH  | COD   | TSS  | NH4  | NO3/NO2 | TDS   | Salinity | Conductivity | TKN  | BOD   |
|-------|------|-----|-------|------|------|---------|-------|----------|--------------|------|-------|
| 0     | 13.9 | 7.5 | 329.8 | 81.6 | 27.6 | 0.2     | 677.8 | 0.7      | 1283.8       | 38.9 | 146.3 |
| 4     | 11.8 | 7.3 | 209.9 | 50.4 | 14.8 | 0.1     | 612.1 | 0.6      | 1159.0       | 41   | 175   |
| 24    | 9.8  | 7.1 | 184.5 | 34.0 | 7.3  | 0.1     | 453.5 | 0.4      | 862.7        | 44.6 |       |
| 48    | 8.0  | 7.2 | 126.0 | 19.1 | 17.6 | 0.0     | 663.7 | 0.6      | 1250.7       | 29.9 |       |
| 168   | 8.5  | 7.2 | 83.5  | 18.1 | 7.8  | 0.1     | 506.3 | 0.5      | 949.0        | 16.7 | 19.8  |
| % Red | 39%  | 5%  | 75%   | 78%  | 72%  | 74%     | 25%   | 29%      | 26%          | 57%  | 87%   |

**Table 23. Summary of spring season wetland treatment performance.**

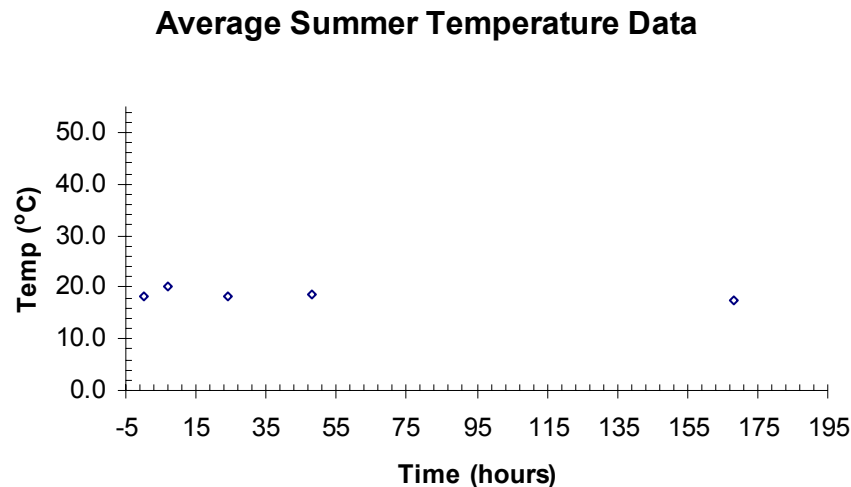
Overall we find a temperature reduction of 39% and a relatively stable pH. As discussed previously COD and BOD performance are acceptable under springtime conditions as well as TSS. Ammonium ion treatment, as compared to winter time conditions is greater, with TKN having marginal improvement over wintertime treatment results. Nitrate/Nitrite, as expected, does not contribute to overall nitrogen within the system and we see a slight decrease in the TDS, Salinity and Conductivity each of which may be related to the settling of solids.

#### **7.4.0 Summer**

Summer time conditions are noted for warm nights and hot dry days and are, within the literature, often considered the optimum season for the treatment of municipal wastewater in a constructed wetland treatment system. As the following data suggests, summer time does not necessarily provide the optimum ambient environmental or wetland conditions for the treatment of wastewater in constructed wetlands. These summertime data were collected over two seasons and consisted of 15 individual experiments.

##### **7.4.1 Temperature**

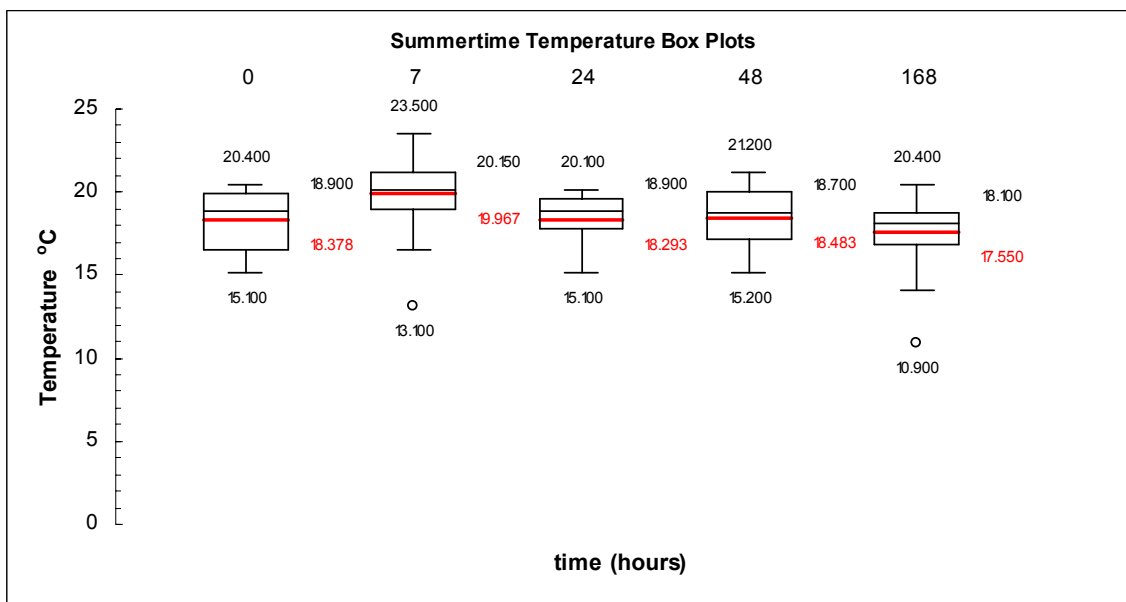
During the summertime, the temperature of the wetland water changes very little as compared to the primary effluent being loaded into the system. Below is a plot of the average temperatures with respect to time for summer season operations.



**Figure 65. Average wetland temperature reduction for summer season.**

From this plot one may note that there exists very little temperature reduction between the primary effluent being introduced into the wetland treatment system and the resulting wetland water temperature at the end of the 168 hour treatment cycle. At times, depending on the ambient air temperature, a slight increase in temperature is realized over the course of the treatment cycle during summertime operating conditions. This is notable as the nutrient dynamics are temperature related and thus the temperature of the primary effluent influences the operating temperature of the wetland system during summer time conditions. In addition, the ambient air temperature does not permit the wetland to cool below the primary effluent temperature.

Taking a look at the temperature box plot all of the summertime temperature data is presented below.

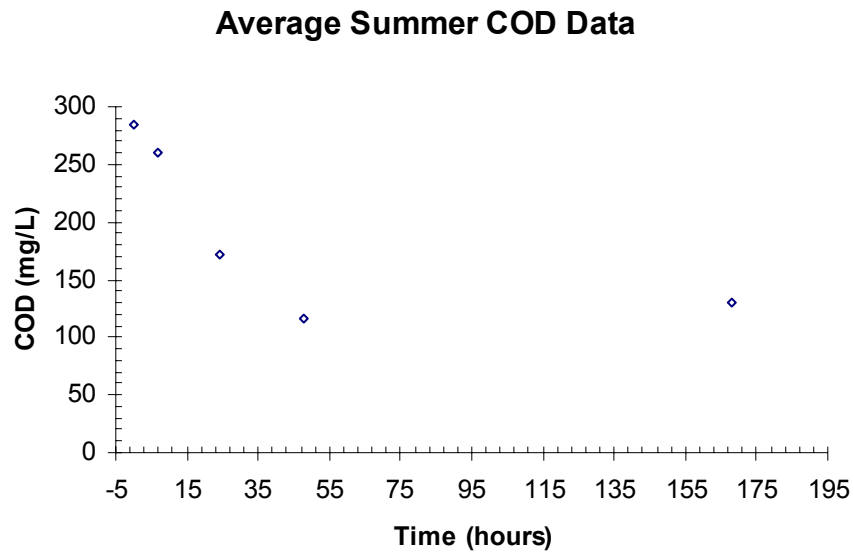


**Figure 66. Box plot of summer temperature data.**

This plot reveals the lack of variability over the course of the treatment cycle as well as revealing extremes in the temperature data. These temperature data suggest that the summer time provides optimum conditions however, as the pollutant and nutrient parameters below are investigated this assumption may not prove valid. As these data show the temperature of the wetland consistently fluctuated around 18°C.

#### 7.4.2 COD and BOD

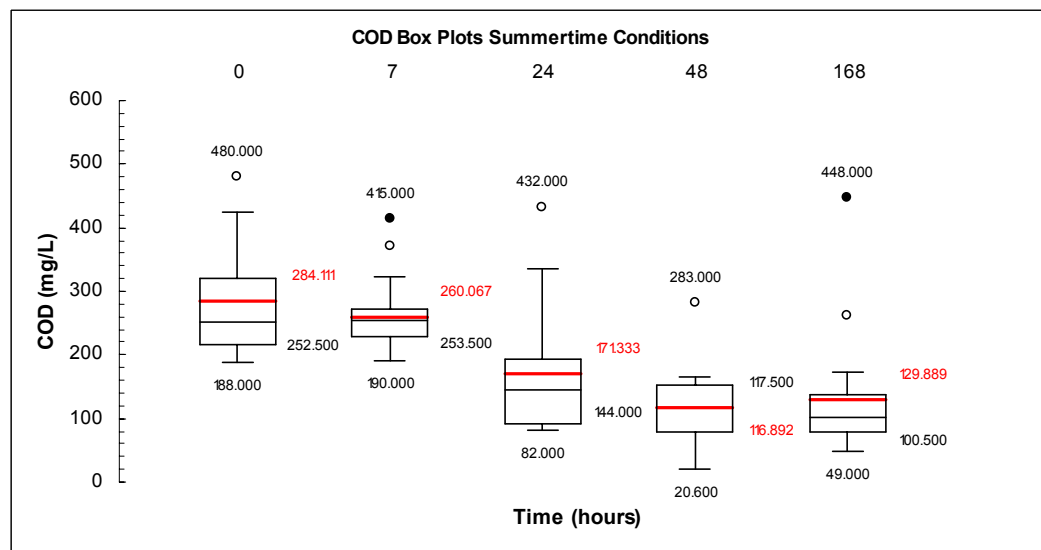
As discussed, COD and BOD are related to the suspension of solids within the wetland treatment system. With the warmer temperatures associated with the wetland and the drop in the viscosity of the water, settling should occur much quicker. However, with the increase in temperature and incident solar irradiation the growth of bacteria and algae increases which may contribute to COD and BOD concentrations. Below is a plot of the average COD concentration with respect to time for the summer season.



**Figure 67. Average wetland COD reduction for summer season.**

These data demonstrate a decrease in COD within the first 24-48 hours with an increase in COD towards the end of the treatment cycle. Minimal treatment is realized after the initial 48 hours. Overall a 54% reduction in COD was determined.

It is instructive to view all the COD in one plot. This is shown below in the COD box plot.

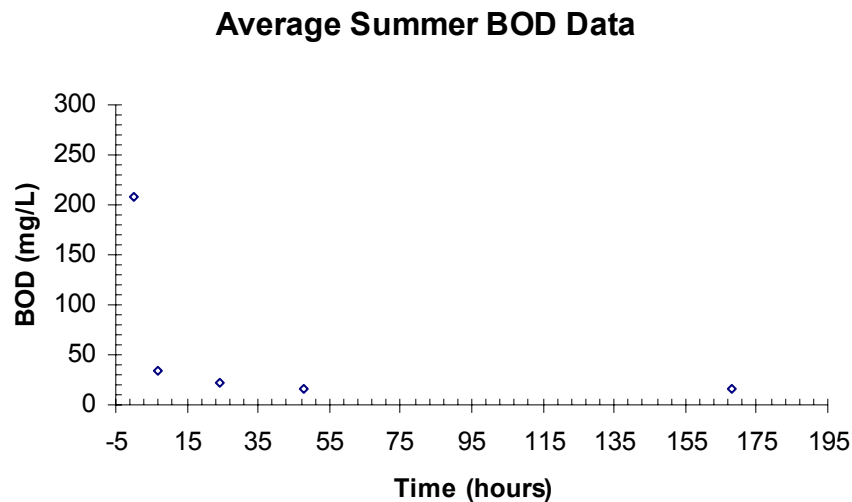




**Figure 68. Box plot of summer COD data.**

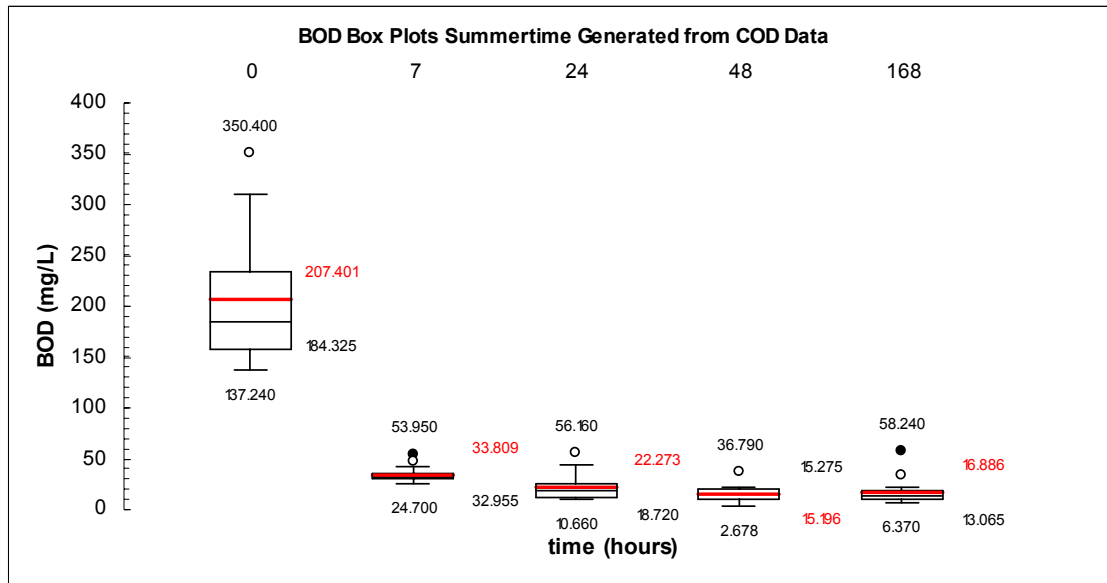
Except for some expected outliers, 50% of the data is concentrated around a defined set of values at each particular sample time. The outliers are thought to be associated to sample error whereby algae and or duckweed was present in the sample at the time of testing.

The BOD treatment reduction is similar to COD. Below is a plot of the overall average concentration of BOD with respect to each particular sample time.



**Figure 69. Average wetland BOD reduction as calculated from COD data.**

BOD actually has a much faster drop in concentration relative to COD however, while not visually evident in this plot, these data show a slight average increase in BOD concentration towards the end of the 168 hour treatment cycle. Below is the box plot for BOD generated from the COD data.

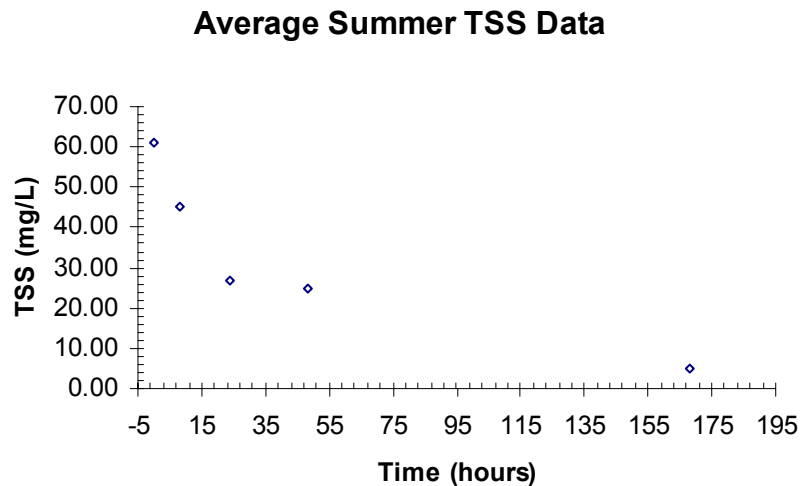


**Figure 70. Box plot of summer BOD data as calculated from COD data.**

As these data suggest there exists the characteristic rapid drop in BOD concentration followed by long term stable concentrations over the course of the remaining treatment time. As these data demonstrated, outliers do exist and have the potential to skew these data and possibly impact the ability to achieve of permissible discharge limits.

### 7.4.3 Summer TSS

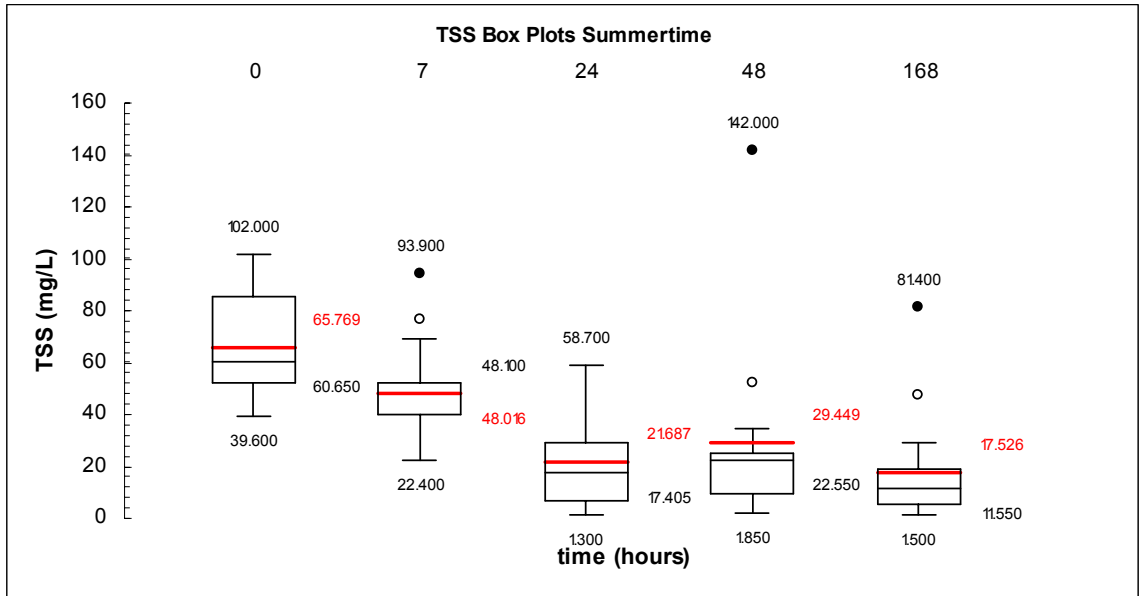
The increase of the wetland operating temperature during the summer time provided interesting results for the treatment of total suspended solids. Below is the plot of the average summer TSS values with respect to time.



**Figure 71. Average wetland TSS reduction for summer season.**

Taking the average data one finds the expected trend in the TSS concentration reducing in the first 24-48 hours with additional reduction in TSS as time progresses. These data plotted demonstrate a drop in TSS within the first 24-48 hours followed by a gradual decrease in TSS concentration as time progresses. Overall, a rapid drop in TSS concentration is found within the first 24 hours to below permit limits with additional reduction in the TSS concentration over the course of the treatment cycle.

All the TSS data during summertime conditions can be found in the box plot below.

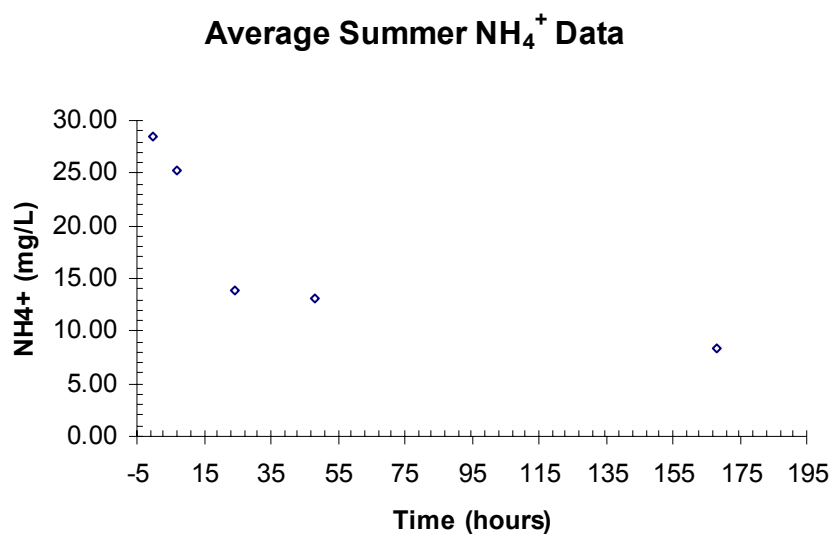


**Figure 72. Box plot of summer TSS data.**

In figure 72, the gradual decrease in TSS concentration is apparent as well as periodic outliers that skew the overall data and can potentially lead to permit violations. The TSS concentrations of certain samples were much greater than others. This is attributed to spikes in the algae population that result from the combination of sunshine, warm water and nutrients found during the summer. The algae is a major contributor to TSS and is not necessarily disruptive internally to the system however, if present in the wetland effluent, the algae can have less than desirable impacts on the receiving body of water and potentially cause TSS permit violations. During the summer time, management of algae is important towards the end of the wetland treatment system and this management can be accomplished using sand filters, vegetation filters or by having the effluent discharge from a location other than the wetland water surface where the highest density of algae is found.

#### **7.4.4 Ammonia as $\text{NH}_4^+$**

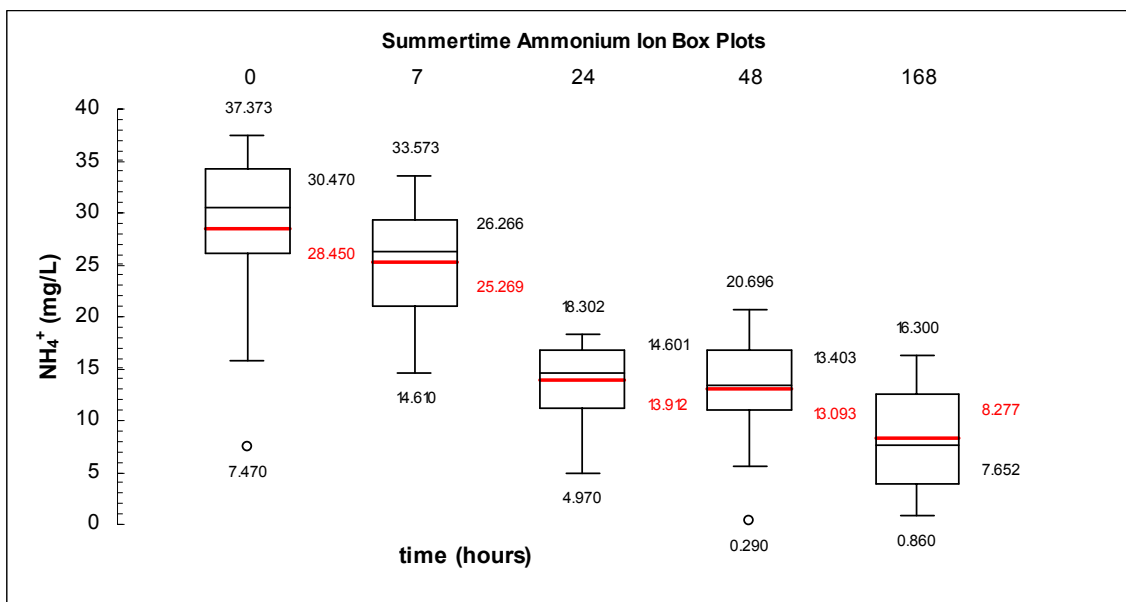
The treatment of ammonia nitrogen (as  $\text{NH}_4^+$ ) within the wetland was assessed during the summertime. The plot below shows the average concentrations of  $\text{NH}_4^+$  with respect to time.



**Figure 73. Average wetland  $\text{NH}_4^+$  reduction for summer season.**

Interestingly this plot is very similar to that of TSS in that there is a rapid decrease in  $\text{NH}_4^+$  within the first 24 hours with treatment subsiding thereafter.

The box plot below provides a visual of all these  $\text{NH}_4^+$  data points.



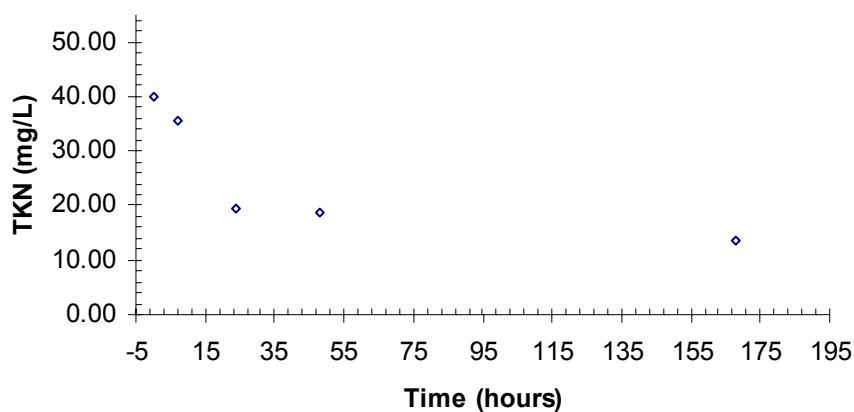
**Figure 74. Box plot of summer  $\text{NH}_4^+$  data.**

The box plot reveals that at the end of the treatment cycle 50% of the data falls between 5 and 14 mg/L of  $\text{NH}_4^+$ . This box plot also reveals a wide range of values for the concentration of ammonia at any particular time during the treatment cycle.

#### 7.4.5 Summer TKN

Similar to ammonia, the treatment of TKN during the summer time is as good as expected. By averaging all the summertime TKN data the plot below was generated.

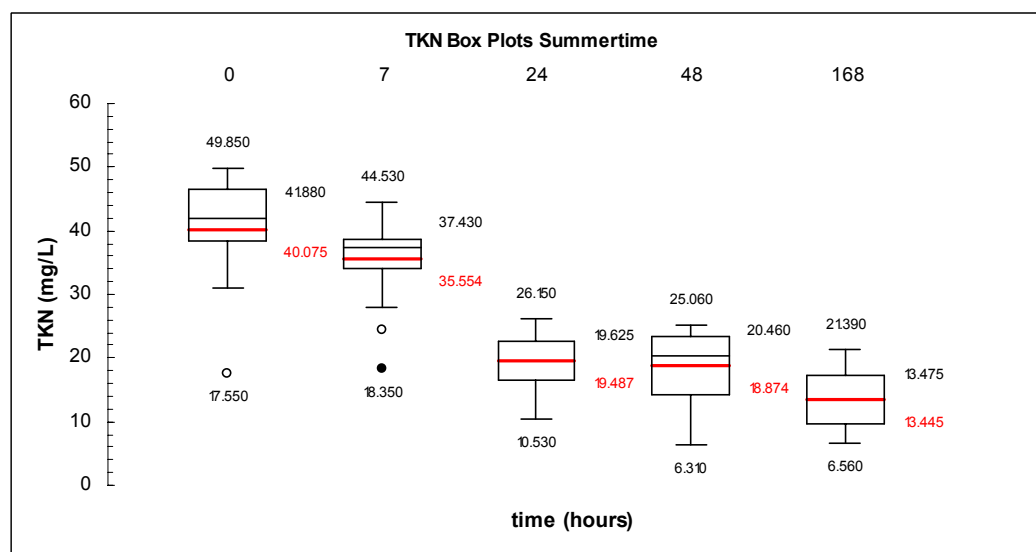
### Average Summer TKN Data



**Figure 75. Average wetland TKN reduction for summer season.**

Here again these data present a similar treatment pattern as with ammonia. The treatment within the wetland is punctuated at approximately 24 hours with little to know reduction in the concentration of TKN thereafter. These data suggest that the maximum treatment ability of TKN in the wetland system is reached within 48 hours.

The dynamic of these TKN data during the summertime are further understood by looking at the box plot below.



**Figure 76. Box plot of summer TKN data.**

As these data in the box plot suggest, the wetland system is periodically able to reduce the TKN concentration to just above 6 mg/L however, 50% of the data falls around 13.5 mg/L after 168 hours. The wetland provided consistent treatment of TKN during the summertime however, the concentration of TKN alone at the end of the treatment cycle was well above the permit limit of 10 mg/L for total nitrogen (TN).

#### **7.4.6 Summertime Summary**

Summertime conditions are characterized by elevated temperatures and extended photoperiods. Summertime is generally considered the optimum season for the treatment of municipal wastewater in a constructed wetland treatment system. These data generated by this work, utilizing an experimental scale constructed wetland system, suggest that the summertime presents significant challenges in the treatment of pollutants. Below is a table showing the averaged data collected under summertime operating conditions.

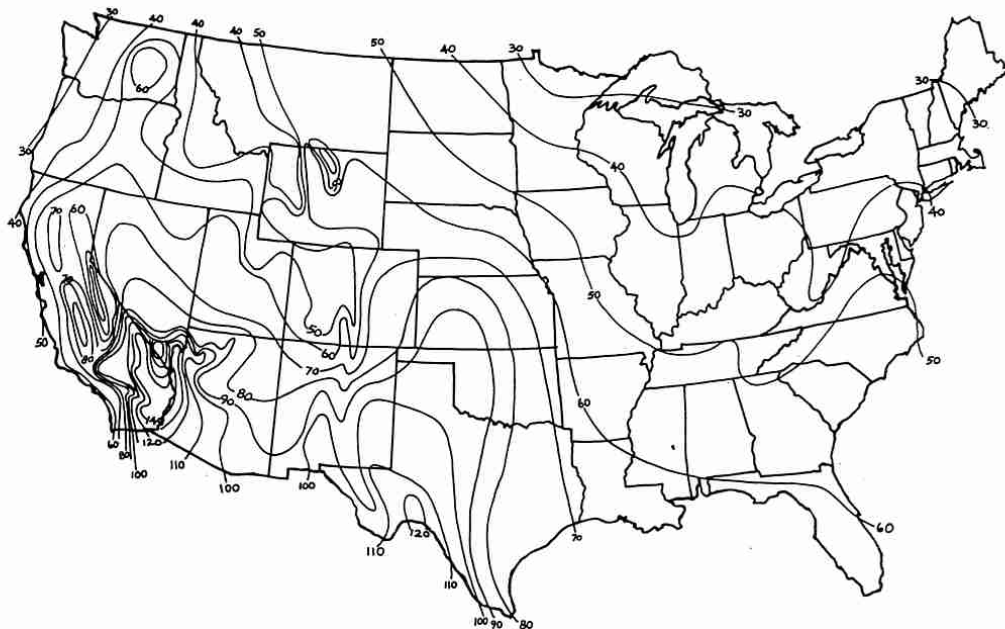
| Hrs    | Temp | pH    | COD | TSS  | NH4   | NO3/NO2 | TDS  | Salinity | Conductivity | TKN   | BOD    |
|--------|------|-------|-----|------|-------|---------|------|----------|--------------|-------|--------|
| 0      | 18.4 | 7.335 | 284 | 65.8 | 28.45 | 0.0539  | 569  | 0.5      | 1085         | 40.08 | 122.09 |
| 7      | 20.0 | 7.154 | 260 | 48.0 | 25.27 | 0.0159  | 560  | 0.5      | 1066         | 35.55 |        |
| 24     | 18.3 | 6.971 | 171 | 22.9 | 13.91 | 0.0165  | 569  | 0.5      | 1084         | 19.49 | 5.75   |
| 48     | 18.5 | 6.964 | 117 | 29.4 | 13.09 | 0.0224  | 605  | 0.5      | 1039         | 18.87 |        |
| 168    | 17.6 | 6.964 | 130 | 17.5 | 8.28  | 0.0304  | 636  | 0.6      | 1133         | 13.45 | 14.62  |
| % Red. | 5%   | 5%    | 54% | 73%  | 71%   | 44%     | -12% | -5%      | -4%          | 66%   | 88%    |

**Table 24. Summary of summer season wetland treatment performance.**

These data reveal that very little changes are found, as expected, with respect to temperature (5% reduction in temperature over 168 hours of treatment). What is interesting however is the lack of COD treatment as compared to the other seasons. Potassium dichromate is a strong oxidant that is used in the COD test. This attacks a large group of compounds. The reduced performance of the wetland for COD levels



suggests that the system may be producing humic compounds at a slightly slower rate than the system is consuming organic compounds within the primary wastewater. This is further substantiated by the 12% increase in total dissolved solids (TDS) and slight increase in conductivity. However, BOD treatment is upwards of 88% suggesting that a large amount of the organic material in the wetland is being treated. Due to the semi-arid conditions found during the summertime in Missoula, organic matter and pollutants are accentuated through the transpiration and evaporation of wetland water. Looking at the national average pan evaporation rate map below and assuming that wetland evapotranspiration is approximately 75% of pan evaporation one may note that the experimental constructed wetland had a daily evapotranspiration rate of approximately 21 mm/day during the summertime (96, 97).



**Figure 77. Map of annual class A pan evaporation data for the United States.** Units are in inches per year. A broad assumption may be made that evaporation only occurs during the growing or summer season (38).

This evapotranspiration found during the summer months concentrates the pollutants and places additional treatment demands on a constructed wetland system. The wetland however, even under these stressful conditions does provide a certain level of treatment. It must be noted that the effects of evapotranspiration may be different between an experimental constructed wetland system and a large scale wetland treatment system.

### ***7.5.0 Seasonal Treatment Kinetics and Modeling***

A goal of this project was to generate seasonal kinetic rate constants for the treatment of certain pollutants and management of certain nutrients in a constructed wetland treatment system treating primary effluent. The results of which may be able to be used in applications throughout western Montana and other regions with similar climatological characteristics. A background on the determination of the rate constants is provided below.

Many natural phenomenon are explained by a general first order kinetics expression in the form of an algebraic equation (98). In terms of wetland treatment systems, engineers have relied on empirical mathematical relationships to predict effluent concentrations rather than relying on kinetic rate constants that describe the underlying chemical principles governing the wetland system (99). Furthermore, the literature has suggested, that wetland chemical kinetics follows first order kinetics based on temperature dependent rate constants (38, 100). This expression is represented below:

$$d[X]/dt = -k[X] \quad (7.1)$$

This equation allows one to understand how the concentration of species X changes with respect to infinitesimally small time changes. Generally there is an initial concentration

$[X]_0$  and a follow on concentration  $[X]_t$  at some designated time  $t$ . Lower case  $k$  is a proportionality constant whose value represents the fractional  $[X]$  that change over time. If  $k$  is small then the change in  $[X]$  over time is slow, if  $k$  is large the change in  $[X]$  over time is relatively fast. The negative sign in the equation represents decay or a decrease in concentration of species  $X$ . This equation is the basis of exponential decay upon which the understanding of the seasonal treatment performance of a constructed wetland system treating primary effluent may be investigated.

From various measurements of  $[X]$  at each relative time  $t$ , an accurate  $k$  value can be determined from the data with units of inverse time. Experimentally with this project, concentrations of criteria pollutants were measured as mg/L at specific times throughout each treatment cycle. Integration of equation 1, shown without proof, provides the following expression that relates the concentration of species  $X$  directly to  $k$ .

$$[X]_{(t)} = [X]_0 e^{-kt} \quad (7.2)$$

An alternate form of this equation is found by taking the logarithm of both sides upon which one gets equation 3 shown below. Taking advantage of the properties of logarithms one finds the expression represented in equation 7.4.

$$\ln [X]_{(t)} = \ln ([X]_0 e^{-kt}) \quad (7.3)$$

$$\ln ([X]_{(t)}/[X]_0) = -k_t t \quad (7.4)$$

With this project, the variables were adjusted to reflect the standard form in the constructed wetland discipline. The adjusted equation is found below.

$$\ln (C_e/C_0) = -k_T t \quad (7.5)$$

In this equation  $C_e$  is the effluent concentration,  $C_o$  is the influent concentration of the pollutant or nutrient (both in mg/L) and  $t$  is the retention time in hours. The proportionality constant ( $-k_T$  in  $\text{hours}^{-1}$ ) is defined as the temperature dependent first order rate constant. Equation 7.6, as shown below was used as the basis to determine the temperature dependent first order rate constants for each respective pollutant investigated and compare that against the actual data.

$$C_e = C_o e^{(-k_T t)} \quad (7.6)$$

With first order kinetics, the half life can be determined for each pollutant using the equation below:

$$t_{1/2} = 0.693/k_T \quad (7.7)$$

where  $k$  is the first order rate constant for the pollutant at some temperature  $T$ . In the following sections, seasonal rate constants for selected pollutants and half-lives are presented. In addition zero, first and second order kinetics are investigated as well in an attempt to determine the most appropriate chemical kinetic interpretation of the treatment characteristics of certain pollutants in a constructed wetland system.

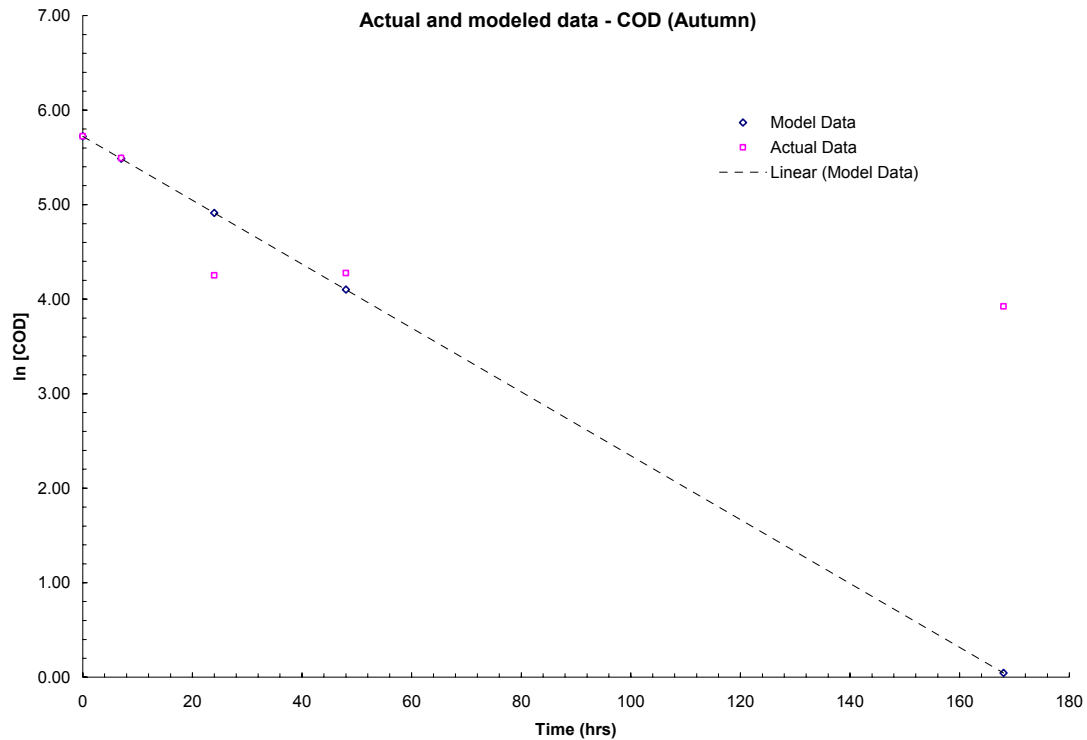
### 7.5.1 Autumn

The temperature dependent rate constants are based on the average temperature of  $12.2^\circ\text{C}$  within the constructed wetland during the autumn experiments and are determined by the first order rate expression. The following table shows again the reduction in pollutant concentrations over time and calculated autumn rate constants ( $k_T$ ) using equation 7.6 and half-life using equation 7.7.

| Time                                 | Temp | pH    | COD   | TSS   | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> /NO <sub>2</sub> | TDS | Salinity | Conductivity | TKN   | BOD    |
|--------------------------------------|------|-------|-------|-------|------------------------------|----------------------------------|-----|----------|--------------|-------|--------|
| 0                                    | 18.0 | 7.403 | 306   | 71.76 | 32.38                        | 0.211                            | 594 | 0.6      | 1150         | 48.88 | 176.38 |
| 7                                    | 15.3 | 7.320 | 243   | 53.88 | 28.33                        | 0.061                            | 590 | 0.6      | 1089         | 42.09 |        |
| 24                                   | 10.2 | 7.191 | 70    | 10.85 | 9.19                         | 0.060                            | 691 | 0.7      | 2355         | 14.31 |        |
| 48                                   | 9.3  | 7.206 | 72    | 7.97  | 9.18                         | 0.085                            | 596 | 0.6      | 1137         | 13.47 |        |
| 168                                  | 8.4  | 7.150 | 51    | 3.59  | 4.70                         | 0.625                            | 598 | 0.6      | 1143         | 7.62  | 4.60   |
| % Red                                | 53%  | 3%    | 83%   | 95%   | 85%                          | -196%                            | -1% | 3%       | 1%           | 84%   | 97%    |
| k <sub>T</sub> (hrs <sup>-1</sup> )  | n/a  | n/a   | 0.03  | 0.05  | 0.03                         | 0.06                             | n/a | n/a      | n/a          | 0.03  | n/a    |
| k <sub>T</sub> (days <sup>-1</sup> ) | n/a  | n/a   | 0.81  | 1.10  | 0.66                         | 1.44                             | n/a | n/a      | n/a          | 0.66  | n/a    |
| t <sub>1/2</sub>                     | n/a  | n/a   | 20.50 | 15.13 | 25.36                        | 11.47                            | n/a | n/a      | n/a          | 25.09 | n/a    |

**Table 25. Autumn first order kinetic data for certain pollutants and nutrients.** This table includes concentration reduction data with respect to time and calculated autumn rate constants and half-life of selective pollutants.

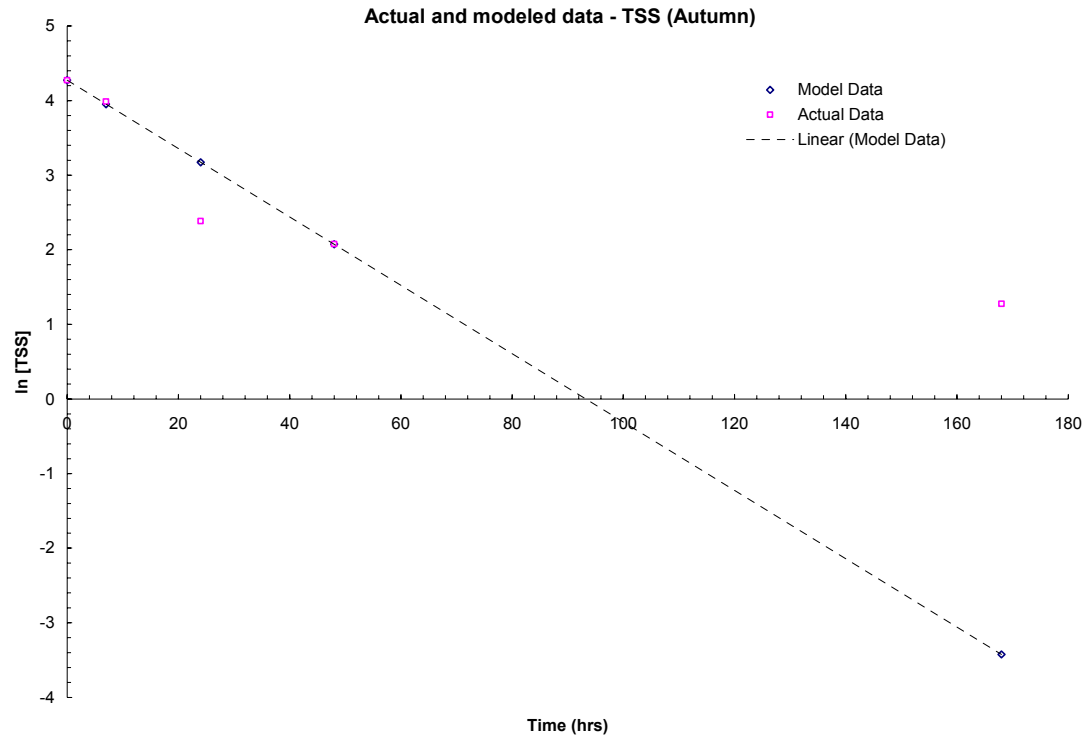
Equation 7.6 was used to model the treatment of pollutants in the fall using the calculated rate constants. The correlation between the modeled data and the actual data using the same initial starting concentration ( $C_0$ ) was good in the early stages of treatment, however the data generated towards the end of the treatment cycle, using the first order rate expression provided by equation 7.6, did not accurately predict the actual experimental data. The following plot demonstrates the correlation between the modeled data and the actual data for COD.



**Figure 78. Actual and modeled first order kinetic data for autumn COD concentrations.**

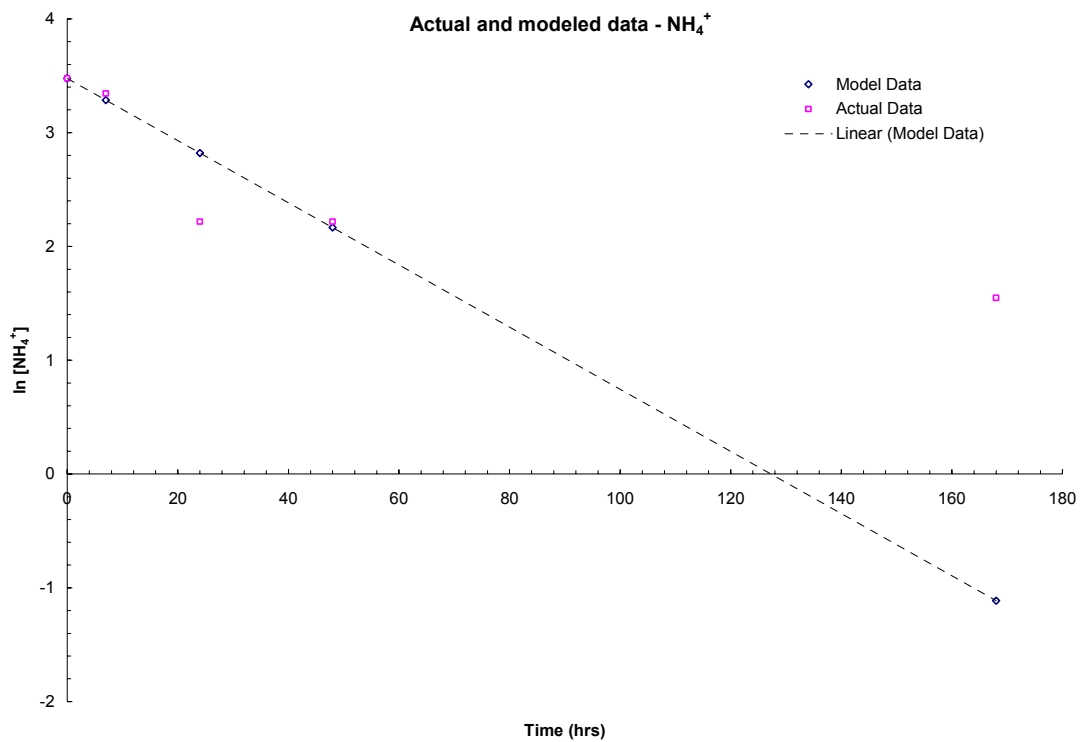
As the figure suggests, there is good correlation with the modeled data and the actual data early on in the treatment process up to approximately 48 hours however, as the treatment progresses the first order rate expression does not accurately predict the concentration at 168 hours of treatment.

Below we have the actual TSS data plotted with the modeled TSS data using the temperature dependent rate constant.



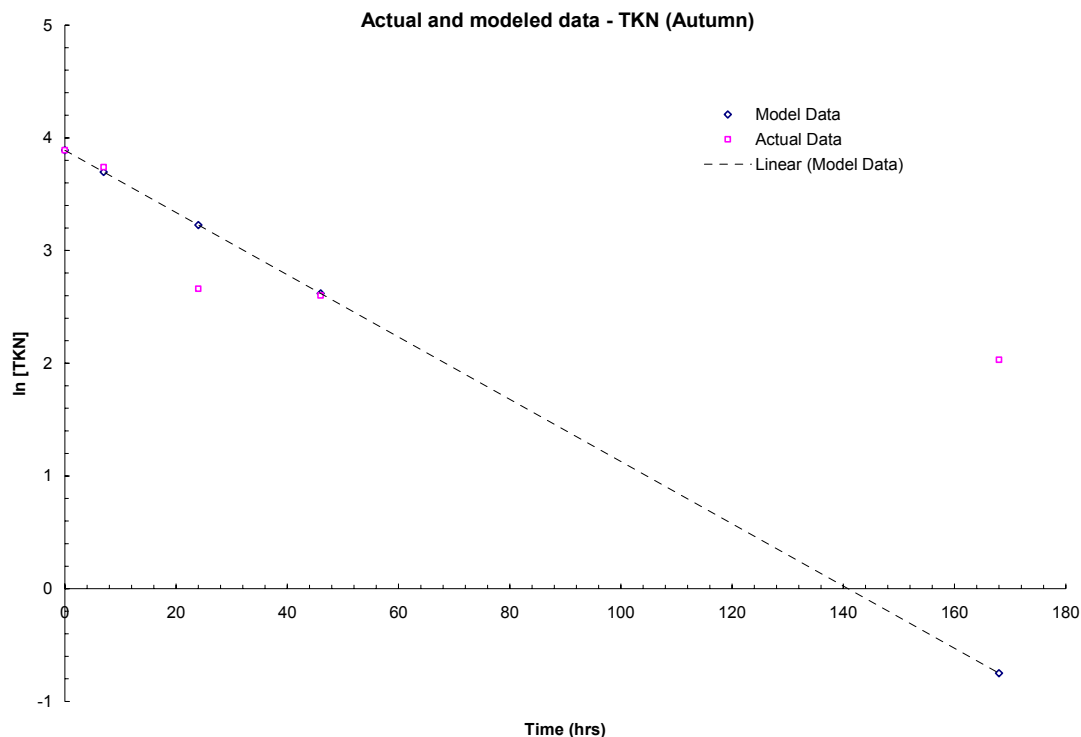
**Figure 79. Actual and modeled first order kinetic data for autumn TSS concentrations.**

Again, as the figure suggests, there is early stage correlation of the actual data with the modeled data, and towards the end of the treatment cycle no correlation between the model and the actual data. A similar result is found with  $\text{NH}_4^+$  and TKN as demonstrated in the plots below.



**Figure 80. Actual and modeled first order kinetic data for autumn  $\text{NH}_4^+$  concentrations.**





**Figure 81. Actual and modeled first order kinetic data for autumn TKN concentrations.**

Again, these plots suggest good correlation with the model during the early stages of treatment, up to approximately 48 hours of treatment, and little to no correlation towards the end of the 168 hours treatment cycle.

### 7.5.2 Winter

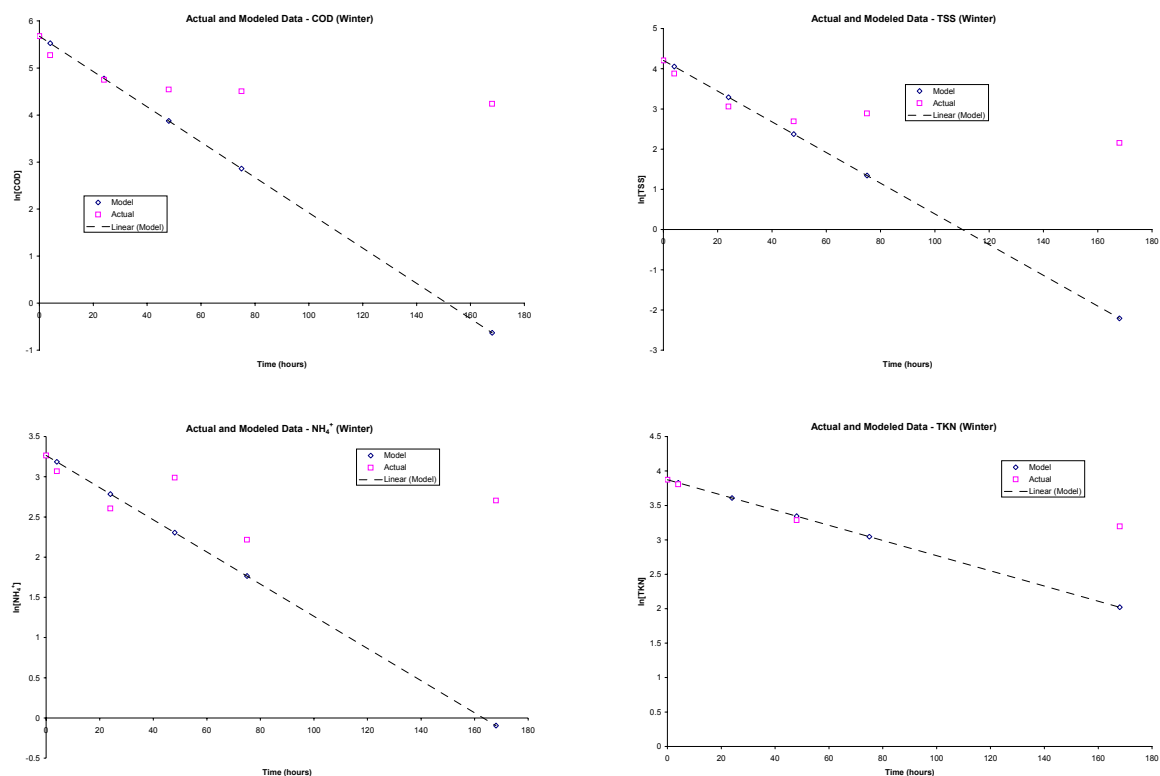
Below is a table showing the treatment of selected pollutants in the experimental constructed wetland during the winter months. Included in this table are the rate constants for selected pollutants.

| Time                        | Temp | pH    | COD   | TSS   | NH4   | NO3/NO2 | TDS | Salinity | Conductivity | TKN   | BOD    |
|-----------------------------|------|-------|-------|-------|-------|---------|-----|----------|--------------|-------|--------|
| 0                           | 15.0 | 7.438 | 292   | 67.29 | 33.11 | 0.254   | 641 | 0.6      | 1246         | 52.17 | 157.23 |
| 4                           | 8.6  | 7.400 | 195   | 48.48 | 21.51 | 0.259   | 615 | 0.6      | 1196         | 44.97 |        |
| 24                          | 5.6  | 7.208 | 116   | 21.30 | 13.55 | 0.020   | 465 | 0.5      | 931          |       |        |
| 48                          | 5.0  | 7.156 | 94    | 14.79 | 19.88 | 0.014   | 549 | 0.5      | 1049         | 26.77 |        |
| 75                          | 3.4  | 7.277 | 90    | 18.02 | 9.18  | 0.309   | 535 | 0.5      | 1063         |       |        |
| 168                         | 3.0  | 7.216 | 69    | 8.63  | 14.95 | 0.142   | 548 | 0.5      | 1054         | 24.44 | 8.30   |
| % Red                       | 80%  | 3%    | 76%   | 87%   | 55%   | 44%     | 14% | 18%      | 15%          | 53%   | 95%    |
| $k_T$ (hrs <sup>-1</sup> )  | n/a  | n/a   | 0.04  | 0.04  | 0.02  | n/a     | n/a | n/a      | n/a          | 0.01  | n/a    |
| $k_T$ (days <sup>-1</sup> ) | n/a  | n/a   | 0.90  | 0.92  | 0.48  | n/a     | n/a | n/a      | n/a          | 0.26  | n/a    |
| $t_{1/2}$                   | n/a  | n/a   | 18.46 | 18.12 | 34.68 | n/a     | n/a | n/a      | n/a          | 62.89 | n/a    |

**Table 26. Winter first order kinetic data for certain pollutants.**

As these data demonstrate, over the course of the 168 hour (7 day) treatment cycle there existed an 80% reduction in the temperature, 76% reduction in COD, 87% reduction in TSS and 95% reduction in BOD. Less efficient reduction of  $\text{NH}_4^+$  was found at 55% and TKN at 53%. TN concentration was determined to be 39.39 mg/L at the end of the treatment cycle which exceeds targeted VNRP discharge limits of 10 mg/L.

Below are a series of plots for COD, TSS,  $\text{NH}_4^+$  and TKN. The plots demonstrate again good correlation between the modeled data and the actual data in the early stages of treatment and significantly less correlation towards the end of the treatment cycle.



**Figure 82. Actual and modeled first order kinetic data for winter.**

### 7.5.3 Spring

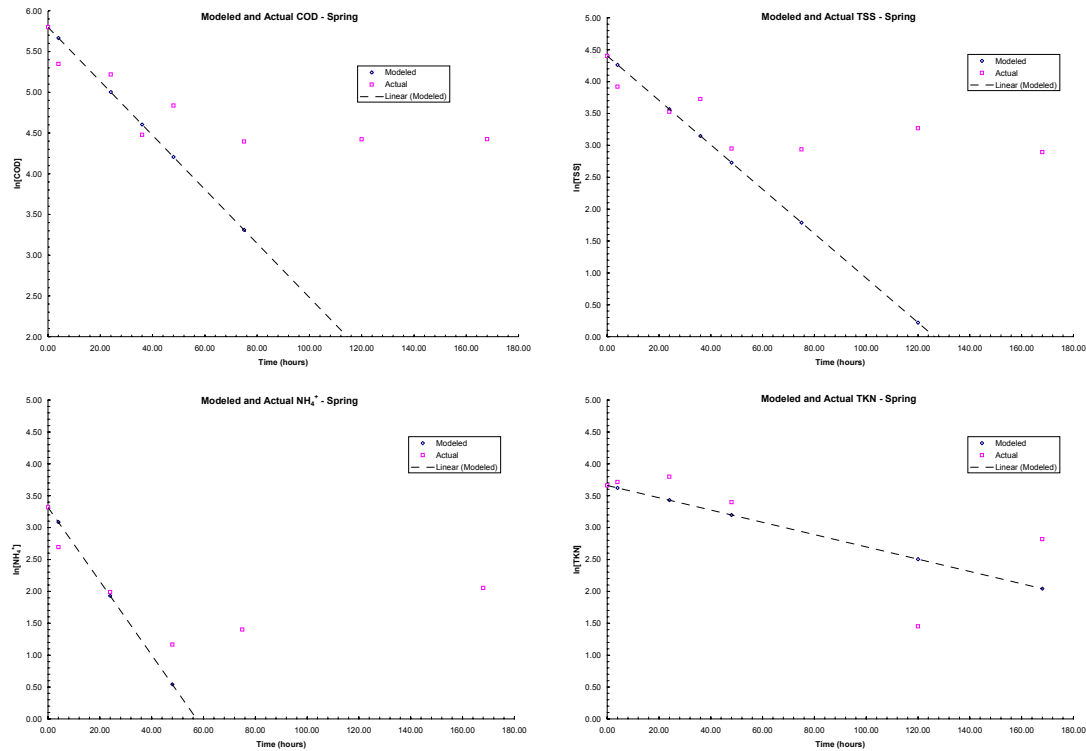
Below is the table showing the reduction over time of the various parameters measured.

| Hrs                                  | Temp  | pH   | COD    | TSS   | NH <sub>4</sub> | NO <sub>3</sub> /NO <sub>2</sub> | TDS    | Salinity | Conductivity | TKN   | BOD    |
|--------------------------------------|-------|------|--------|-------|-----------------|----------------------------------|--------|----------|--------------|-------|--------|
| 0.00                                 | 13.91 | 7.53 | 329.78 | 81.55 | 27.61           | 0.23                             | 677.78 | 0.66     | 1283.78      | 38.87 | 146.34 |
| 4.00                                 | 11.84 | 7.30 | 209.91 | 50.40 | 14.81           | 0.10                             | 612.09 | 0.58     | 1159.00      | 41.00 | 175.00 |
| 24.00                                | 9.83  | 7.14 | 184.50 | 33.98 | 7.34            | 0.10                             | 453.50 | 0.42     | 862.67       | 44.63 |        |
| 48.00                                | 8.03  | 7.17 | 126.00 | 19.12 | 17.62           | 0.04                             | 663.67 | 0.63     | 1250.67      | 29.91 |        |
| 168.00                               | 8.52  | 7.18 | 83.50  | 18.06 | 7.80            | 0.06                             | 506.33 | 0.47     | 949.00       | 16.75 | 19.75  |
| % Red                                | 0.39  | 0.05 | 0.75   | 0.78  | 0.72            | 0.74                             | 0.25   | 0.29     | 0.26         | 0.57  | 0.87   |
| k <sub>T</sub> (hrs <sup>-1</sup> )  | n/a   | n/a  | 0.03   | 0.03  | 0.06            | n/a                              | n/a    | n/a      | n/a          | 0.01  | n/a    |
| k <sub>T</sub> (days <sup>-1</sup> ) | n/a   | n/a  | 0.8    | 0.84  | 1.39            | n/a                              | n/a    | n/a      | n/a          | 0.23  | n/a    |
| t <sub>1/2</sub>                     | n/a   | n/a  | 20.8   | 19.89 | 11.98           | n/a                              | n/a    | n/a      | n/a          | 71.72 | n/a    |

**Table 27. Spring first order kinetic data for certain pollutants.**

The average temperature of the wetland water during the spring was 10.43°C. The respective rate constants are based on this average temperature. The rate constants were

again used to generate modeled data using the first order rate expression found in equation 7.6 and this modeled data was compared to the actual data in the series of plots below.



**Figure 83. Actual and modeled first order kinetic data for spring.** Using equation 7.6 the following plots were generated. The plots show the modeled data using the respective rate constant ( $\text{hrs}^{-1}$ ) and the actual data plotted with respect to time.

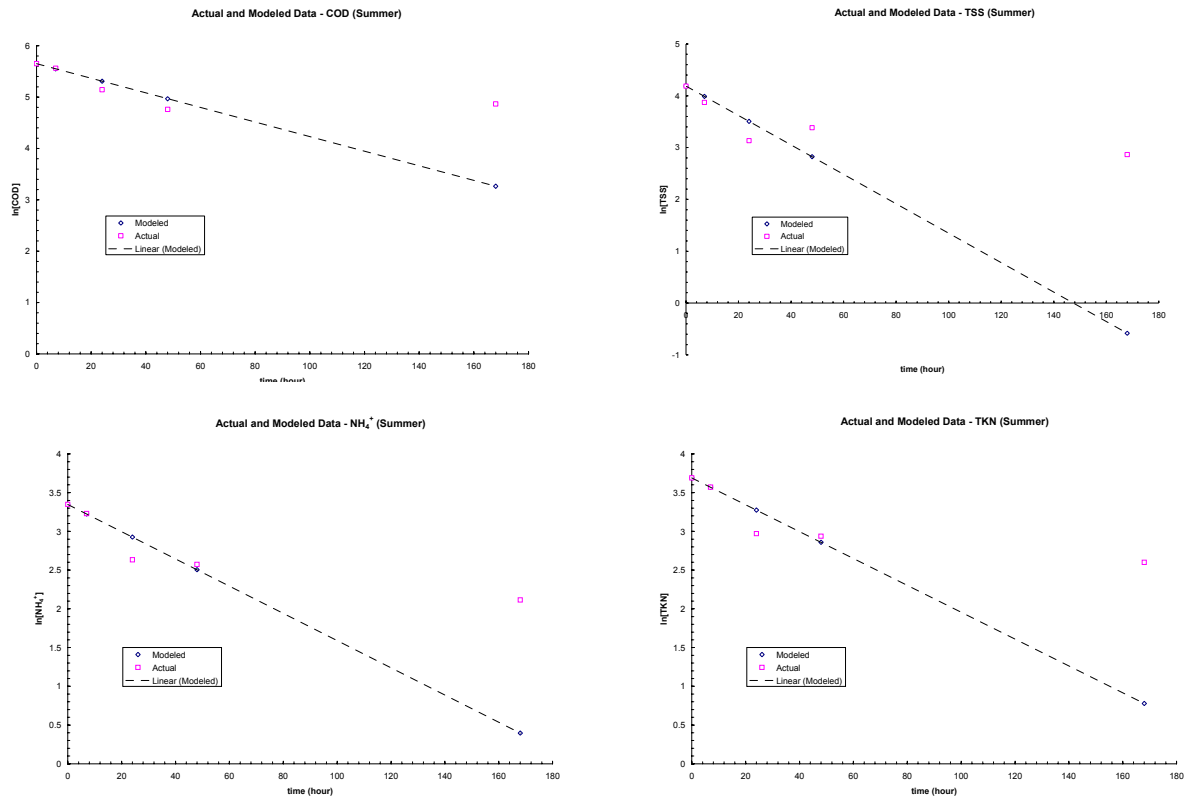
As these plots suggest, again there is fairly good correlation with the model in the early stages of treatment and very little correlation after approximately 48 hours. The modeled data and the actual data with respect to  $\text{NH}_4^+$  are profoundly different over the course of the 168 hour treatment cycle. The one exception, as demonstrated above, to this pattern of later stage data found between the modeled and actual data is TKN, whereby the actual data correlates well with the modeled data over the course of the 168 hour treatment cycle.

## 7.5.4 Summer

Below is the summary data for summertime treatment conditions. Also included in the table are the temperature dependent rate constants. The average temperature of the wetland water during summertime operations was 18.5°C.

| Hrs                         | Temp | pH    | COD   | TSS   | NH <sub>4</sub> | NO <sub>3</sub> /NO <sub>2</sub> | TDS  | Salinity | Conductivity | TKN   | BOD    |
|-----------------------------|------|-------|-------|-------|-----------------|----------------------------------|------|----------|--------------|-------|--------|
| 0                           | 18.4 | 7.335 | 284   | 65.8  | 28.45           | 0.0539                           | 569  | 0.5      | 1085         | 40.08 | 122.09 |
| 7                           | 20.0 | 7.154 | 260   | 48.0  | 25.27           | 0.0159                           | 560  | 0.5      | 1066         | 35.55 |        |
| 24                          | 18.3 | 6.971 | 171   | 22.9  | 13.91           | 0.0165                           | 569  | 0.5      | 1084         | 19.49 | 5.75   |
| 48                          | 18.5 | 6.964 | 117   | 29.4  | 13.09           | 0.0224                           | 605  | 0.5      | 1039         | 18.87 |        |
| 168                         | 17.6 | 6.964 | 130   | 17.5  | 8.28            | 0.0304                           | 636  | 0.6      | 1133         | 13.45 | 14.62  |
| % Red.                      | 5%   | 5%    | 54%   | 73%   | 71%             | 44%                              | -12% | -5%      | -4%          | 66%   | 88%    |
| $k_T$ (hrs <sup>-1</sup> )  | n/a  | n/a   | 0.014 | 0.028 | 0.018           | n/a                              | n/a  | n/a      | n/a          | 0.173 | n/a    |
| $k_T$ (days <sup>-1</sup> ) | n/a  | n/a   | 0.341 | 0.681 | 0.422           | n/a                              | n/a  | n/a      | n/a          | 0.416 | n/a    |
| $t_{1/2}$                   | n/a  | n/a   | 48.82 | 24.41 | 39.45           | n/a                              | n/a  | n/a      | n/a          | 39.97 | n/a    |

**Table 28. Summer first order kinetic data for certain pollutants.**



**Figure 84. Actual and modeled first order kinetic data for summer.**

Again, during the summer season these data suggest good correlation during the early stages of the treatment process using the rate constants generated with little to no correlation beyond approximately 48 hours of treatment.

### **7.5.5 Comparison of Zero, First and Second order Kinetics**

Due to the uncertainty of strictly assuming first order kinetics as the underlying chemical principle governing wetland treatment systems, the following comparison is presented between the whole number kinetic orders.

First order kinetics is described above. The following is a discussion of zero and second order kinetics. Zero order reactions have the following concentration and time relationship.

$$C_o - C_e = kt \quad (7.8)$$

Temperature dependent rate constants were determined by rearranging equation 7.8 and solving for the rate constant (k) at respective times (t) and concentrations ( $C_e$ ). Using the zero order rate constants, a zero order plot of  $C_e$  with respect time was made and compared to actual data for certain pollutants. Second order kinetics uses the following concentration and time relationship.

$$1/C_e - 1/C_o = kt \quad (7.9)$$

A second order temperature dependent rate constant was determined by rearranging equation 7.9 and solving for k at respective times t and concentrations  $C_e$ . Using the second order rate constant and the initial concentration  $C_o$ , a second order plot of  $1/C_e$  with respect to time was made and compared to the actual data for certain pollutants.

Furthermore, as the first order plots suggest from above, the first order kinetics is demonstrated in the early stages of the treatment cycle but not in the later stages. Therefore, the later stage data was removed and regression analysis was conducted to see how well the actual data fit as compared to the chemical kinetics. The same analysis was conducted with the later stage data included. A summary of the results is presented below in the following table.

| Fall                    | COD                                      |   | TSS                                      |   | NH <sub>4</sub> <sup>+</sup>             |   | TKN                                      |  |
|-------------------------|--|---|--|---|--|---|--|--|
|                         | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed  |
| Zero                    | 0.4330                                   | 0.787                                   | 0.4424                                   | 0.8138                                  | 0.5127                                   | 0.7895                                  | 0.4992                                   | 0.8221                                   |
| First                   | 0.5366                                   | 0.7788                                  | 0.6828                                   | 0.8725                                  | 0.6977                                   | 0.7858                                  | 0.6724                                   | 0.8315                                   |
| Second                  | 0.6889                                   | 0.7642                                  | 0.9582                                   | 0.9381                                  | 0.8999                                   | 0.7806                                  | 0.8754                                   | 0.8434                                   |
| Winter                  | COD                                      |   | TSS                                      |   | NH <sub>4</sub> <sup>+</sup>             |   | TKN                                      |  |
|                         | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value*<br>outlier removed |
| Zero                    | 0.5053                                   | 0.6747                                  | 0.5328                                   | 0.6706                                  | 0.285                                    | 0.634                                   | 0.6802                                   | 0.9963                                   |
| First                   | 0.661                                    | 0.774                                   | 0.742                                    | 0.7143                                  | 0.231                                    | 0.6574                                  | 0.7088                                   | 0.9991                                   |
| Second                  | 0.8206                                   | 0.8554                                  | 0.9106                                   | 0.7143                                  | 0.1711                                   | 0.6694                                  | 0.7409                                   | 0.9995                                   |
| *only three data points |  |   |  |   |  |   |  |  |
| Spring                  | COD                                      |   | TSS                                      |   | NH <sub>4</sub> <sup>+</sup>             |   | TKN                                      |  |
|                         | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed  |
| Zero                    | 0.4995                                   | 0.736                                   | 0.4749                                   | 0.7168                                  | 0.2481                                   | 0.6474                                  | 0.7383                                   | 0.9054                                   |
| First                   | 0.5794                                   | 0.7853                                  | 0.5475                                   | 0.8166                                  | 0.1782                                   | 0.7804                                  | 0.5385                                   | 0.9037                                   |
| Second                  | 0.6185                                   | 0.6964                                  | 0.5558                                   | 0.4426                                  | 0.0777                                   | 0.7626                                  | 0.3199                                   | 0.5106                                   |
| Summer                  | COD                                      |   | TSS                                      |   | NH <sub>4</sub> <sup>+</sup>             |   | TKN                                      |  |
|                         | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed | R <sup>2</sup> value<br>outlier included | R <sup>2</sup> value<br>outlier removed  |
| Zero                    | 0.4600                                   | 0.9652                                  | 0.489                                    | 0.6279                                  | 0.6188                                   | 0.8232                                  | 0.5706                                   | 0.8077                                   |
| First                   | 0.4644                                   | 0.9902                                  | 0.6071                                   | 0.5803                                  | 0.7613                                   | 0.8371                                  | 0.6846                                   | 0.8153                                   |
| Second                  | 0.4525                                   | 0.9937                                  | 0.7255                                   | 0.4958                                  | 0.8945                                   | 0.8515                                  | 0.8082                                   | 0.8224                                   |

**Table 29. Zero, first and second order kinetics regression analysis.** This regression analysis compares kinetic order of treatment of selected pollutants.

As these data suggest, second order kinetics more closely describes the chemical nature of constructed wetland treatment than does either first or zero order.

### 7.6.0 Seasonal Treatment Conclusions

The treatment of criteria pollutants in a constructed wetland is challenging regardless of the season. The spring and the fall present the most favorable conditions for the treatment of municipal wastewater in a constructed wetland. The summertime as

discussed has limitations related to the concentration of pollutants. The primary issues with summertime treatment performance are evapotranspiration and biomass production. Evapotranspiration, the combined evaporation and uptake of water by plants, reduces the volume of water in the wetland system over the course of the treatment cycle. This reduction in water volume causes the concentration of pollutants to increase over the course of the treatment cycle. The large amount of sunshine and nutrient rich environment creates for ideal conditions for biomass production most notably in the form of algae. In addition, biomass is also created through the nitrification process where by 0.131 g of biomass are created for every 1 g of  $\text{NH}_4^+$  nitrified. This production of biomass contributes to TSS and BOD concentrations and the cell tissues, through ammonification, contribute additional  $\text{NH}_4^+$  to the system placing additional demands on the ability of the wetland to meet permissible discharge guidelines.

The discharge permit for municipalities does not change with the seasons. The permit requirements for wastewater treatment plants in Montana are found in the table below.

| Missoula WWTP Permit Limits (30 day) |                      |
|--------------------------------------|----------------------|
| Criteria                             | Concentration (mg/L) |
| BOD                                  | 25                   |
| TSS                                  | 30                   |
| TN                                   | 10                   |
| TP*                                  | 1                    |
| *Target level under VNRP             |                      |

**Table 30. Montana DEQ permissible 30 day discharge limits.**

Critically evaluating the seasonal data with respect to these discharge permits one may find that BOD and TSS 30 day permit limits are achievable whereas the wetland violates TN permit limits in each season. Below is a chart showing average concentrations of



criteria pollutants at the end of the 168 hour treatment cycle relative to the permit limits regulated by the Montana Department of Environmental Quality.

| Values in mg/L |        |        |        |        |               |
|----------------|--------|--------|--------|--------|---------------|
| Criteria       | Autumn | Winter | Spring | Summer | 30 day Permit |
| BOD            | 4.60   | 8.30   | 19.80  | 14.62  | 25.00         |
| TSS            | 3.59   | 8.63   | 18.10  | 17.50  | 30.00         |
| TN             | 12.32  | 39.39  | 24.50  | 21.37  | 10.00         |

**Table 31(a). Comparison of seasonal treatment performance with permit limits.**

| Experimental wetland performance - Seasonal Summary |      |    |     |     |                              |                                      |        |             |                  |     |     |
|---|------|----|-----|-----|------------------------------|--------------------------------------|--------|-------------|------------------|-----|-----|
| % Removal or decrease                               | Temp | pH | COD | TSS | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> /NO <sub>2</sub> (1) | TDS(2) | Salinity(2) | Conductivity (2) | TKN | BOD |
| Fall  | 53%  | 3% | 83% | 95% | 85%                          | n/c                                  | n/c    | 3%          | 1%               | 84% | 97% |
| Winter  | 80%  | 3% | 76% | 87% | 55%                          | 44%                                  | 14%    | 18%         | 15%              | 53% | 95% |
| Spring  | 39%  | 5% | 75% | 78% | 72%                          | 74%                                  | 25%    | 29%         | 26%              | 57% | 87% |
| Summer  | 5%   | 5% | 54% | 73% | 71%                          | 44%                                  | -12%   | -5%         | -4%              | 66% | 88% |

(1) initial concentrations were less than 1 ppm

(2) negative sign indicates an increase

**Table 31(b). Comparison of seasonal percent removal of selected pollutants and nutrients.**

As may be noted from the tables above BOD and TSS performance is quite good with respect to the permit limits whereas the TN permit limit is violated in each of the four seasons. Overall, autumn provides the best seasonal conditions with respect to treatment performance. TN values are determined by adding the NH<sub>4</sub><sup>+</sup> and TKN values with TKN contributing the slightly less than one and one half the amount of NH<sub>4</sub><sup>+</sup>.

## 8.0.0 Wetland Effluent Re-use

### Overview:

This work has determined that constructed wetlands provide for the reduction in pollutant concentration and management of nutrient concentrations from municipal wastewaters. It is also understood that crops require certain nutrient levels and certain water applications for optimum growth and productivity. Irrigation is a method by which the water requirements of a certain crops can be highly regulated and controlled.

Traditionally, nutrient needs for crops are provided by the mechanical application of fertilizers which supplement the existing soil nutrient profile. In addition, certain crops have been demonstrated to be grown as “industrial” or energy crops and also certain municipalities, depending on population, have a relatively constant annual supply of nutrients through a centralized wastewater collection system. Those same municipalities, in general, provide services to citizens with certain equipment that requires the use of diesel fuel. Therefore, this work has concluded that it may be beneficial to design a constructed wetland to reduce the concentration of nutrients in primary effluent to levels that are appropriate for the wetland effluent to serve as both irrigation water and a nutrient (fertilizer) source for an energy crop that, upon chemical conversion, provides a fuel for use by the municipality. In addition, this work provides for a means to analyze and screen the technical and economic feasibility through a simple quantitative sizing and predictive model and a simple return on investment (ROI) calculation. The following discussion provides a link between municipal fuel consumption and the size of the constructed wetland required to provide sufficient water and nutrients in the production of this fuel. This model may serve as a tool by which municipalities may rapidly asses

the feasibility of incorporating a constructed wetland and industrial crop irrigation system into their treatment scheme. The constructed wetland design model is developed to provide for both the water volume and nutrient concentrations for an industrial canola oilseed crop and can be used, by substituting different crop specific constants, for other energy or forage crops. The crop is then harvested and processed for revenue or other use by the municipality. Incorporated into this analysis is an understanding of the requisite nutrient loading rates into the wetland system, the necessary land requirements of the wetland to meet both crop irrigation requirements and management of the crop nutrient requirements, and the land requirements for the necessary crop production. The discussion focuses on a case study using the City of Missoula in Montana. This model has the most utility when an industrial oilseed crop is grown, harvested and processed to produce diesel fuel that can be used by the municipality. The model may not be appropriate, however, when more definitive predictive data are required such as may be the case for large scale and expensive construction projects or other tax revenue supported public projects.

### ***8.1.0 Municipal Assumptions and Fuel Production Model***

The City of Missoula was chosen for convenience as the municipality for the discussion of the model development. This model has broad feasibility analysis applications to municipalities between populations of 1,000 to 500,000. Depending on the goals of the community, however, significant land requirements may be necessary. While each community that may use this model will inevitably be unique, the same general questions will need to be asked and answered. As a guideline, the model development is based on the following questions:

- 1) What are the annual gallons of diesel ( $G_Y$ ) fuel consumed by the municipality?
- 2) What is the suitable oilseed crop for the climatic region; including
  - a. What is the growing season of the crop in days ( $D$ )?
  - b. What is the estimated yield per acre of the crop ( $Y_c$ ) in pounds?
  - c. What is the water requirement ( $W_g$ ) in gallons of the crop during the growing season?
  - d. What is the natural precipitation rate ( $P_g$ ) in gallons for the region during the growing season?
  - e. What is the nitrogen requirement of the crop ( $N_R$ ) in kg/acre?
  - f. What is the phosphorus requirement of the crop ( $P_R$ ) in kg/acre?
- 3) What is the pretreatment step prior to the constructed wetland?
- 4) What is the total nitrogen concentration ( $N_P$ ) in the effluent from the pretreatment system?
- 5) What is the total phosphorus concentration ( $P_P$ ) in the effluent from the pretreatment?

Answering Question 1 and determining the volume of diesel fuel consumed per year ( $G_Y$ ) for a particular municipality generally involves communication with the City Fleet Manager or an equivalent position in the city administration that either purchases or manages the fuel or vehicle requirements for a particular city. The volume of diesel fuel may loosely correlate to the population though no extensive investigation of this correlation was conducted and it is best to consult directly with the city in determining the annual diesel fuel consumption.

With  $G_Y$  determined, focused can be placed on determining the most appropriate crop and the crop yield ( $Y_C$ ) under irrigation. With oilseeds, vegetable oil content ( $O_C$ ) needs to be considered and understood as the vegetable oil must be extracted from the oilseed crop selected. With oilseeds, the model assumes that a small scale oilseed press is utilized for the recovery of vegetable oil. With these types of small scale decentralized oilseed crush systems, the extraction efficiency ( $E_e$ ) is generally 94%, meaning 94% of the available oil in the seed is recovered. Processing losses are realized through the handling and crushing of the oilseed. This is considered shrink ( $S$ ) and is generally calculated at 2% of the total pounds of seed processed. The fuel produced per acre ( $F_p$ ) in gallons is therefore determined by the following equation:

$$F_p = \{[(Y_C)(O_C)E_e(1-S)]/\Phi\}(F_C) \quad (8.1)$$

where  $\Phi$  is the conversion of pounds of oil to gallons of oil (7.8 pounds of oil per gallon of oil) and  $F_C$  is the conversion efficiency of vegetable oil to diesel fuel which is generally 95% with smaller scale batch type processing systems that are assumed to be used. The acres of cropland necessary ( $A_C$ ) are then determined by the following equation:

$$A_c = G_Y/F_p \quad (8.2)$$

The water requirements will vary depending on the crop. Water requirements are first determined in acre inches ( $W_{ain}$ ) with one acre inch of precipitation equivalent to approximately 27,154 gallons of water. This conversion is designated as  $\theta$  in the following equations and has units of gallons per acre-inch. The volume of water

necessary for the crop production ( $W_g$ ), in units of gallons, can be determined by the following equation:

$$W_g = W_{ain}A_c(\theta) \quad (8.3)$$

The water requirement necessary for crop production ( $W_g$ ) as determined by equation 3 is not, however, the irrigation requirement. The daily irrigation requirement ( $I_D$ ) must account for natural precipitation ( $P_g$ ), which is reported in acre-inches and converted to gallons, present during the growing season ( $D$ ). The daily irrigation requirements can be determined using the following equation:

$$I_D = [(W_g - P_g)/D]I_E \quad (8.4)$$

where  $I_E$  is the irrigation efficiency expressed as a fractional increase over 100% of the irrigation requirements. This value will vary depending on the type of irrigation equipment utilized. Below is a table showing some relative irrigation efficiencies for various methods.

| Irrigation Efficiency <sup>(80)</sup> |                  |             |
|---------------------------------------|------------------|-------------|
| Type of Irrigation System             | Efficiency Range | $I_E$       |
| Flood                                 | 0.7-0.8          | 1.30 - 1.20 |
| Wheelline                             | 0.80-0.90        | 1.20-1.10   |
| Pivot                                 | 0.90-0.95        | 1.10-1.05   |
| Drip                                  | 0.95             | 1.05        |

**Table 32. Irrigation efficiencies for various methods of irrigation.**

Through the above equations the daily irrigation requirement relates to the acres of crop land necessary to produce a sufficient amount of diesel fuel.

### **8.2.0 Wetland Design Model**

The wetland design model developed here incorporates the design parameters as developed by Dr. R.A. Gearheart, Ph.D., P.E. and presented at the Constructed Wetlands Workshop at Humboldt State University in Arcata, California in 2001 (101).

The development of the appropriate size for the wetland for the feasibility modeling proposed here is accomplished by starting with the daily nitrogen fertilizer requirements ( $N_D$ ) and the daily irrigation requirements ( $I_D$ ), the latter of which is determined by Equation 8.4. The fertilizer requirements are based on the needs of the crop of choice and can be determined by the following equation:

$$N_D = (N_R A_C)/D \quad (8.5)$$

where  $N_R$  is the nitrogen fertilizer requirements in kilograms per acre for the growing season and  $A_C$  is the acres of crop production and  $D$  is the number of days in the crop's growing season. Taking the daily fertilizer requirements ( $N_D$ ) and combining it with the daily irrigation requirements ( $I_D$ ), one can determine the concentration of nitrogen required in the effluent ( $N_{WE}$ ) in mg/L from the equation below:

$$N_{WE} = [(N_D)(1 \times 10^6)(0.264)]/I_D \quad (8.6)$$

where  $1 \times 10^6$  is the unit conversion between milligrams and kilograms and 0.264 is the unit conversion between gallons and liters. The units of  $N_{WE}$  are, therefore, mg/L.

Equation 6 provides a very important number as this is the targeted concentration of the total nitrogen concentration of the effluent from the constructed wetland. This, perhaps, is the cornerstone value determined within the model.

The next calculation addressed is the flow rate through the wetland ( $W_{FR}$ ). The flow rate through the wetland is a function of the  $I_D$  (converted to units of  $m^3/day$ ) and the

evapotranspiration buffer coefficient of the climatic region ( $ET_B$ ) with  $W_{FR}$  determined by the equation below:

$$W_{FR} = (I_D)(ET_B) \quad (8.7)$$

where  $ET_B$  is a unit-less number with a fractional value over one hundred percent of the volume of water entering the wetland relative to the actual water exiting the wetland.

The  $ET_B$  will vary and is region specific.

With the  $W_{FR}$  determined the next step is to determine the necessary size of the wetland in hectares ( $W_{ha}$ ) to achieve the irrigation and fertilization goals for the particular crop. This is determined by the following equation:

$$A_{ha} = [(W_{FR})(N_P)(1 \times 10^{-6})(1000)]/N_L \quad (8.8)$$

Where  $N_P$  is the nitrogen concentration from the pretreatment step in milligrams per liter,  $N_L$  is the nitrogen loading rate to the wetland in kilograms per hectare per day as determined from the experimental data generated by this wetland project,  $1 \times 10^{-6}$  is the conversion of milligrams to kilograms, and 1000 is the conversion between liters (L) and cubic meters ( $m^3$ ). The area of the wetland as calculated ( $A_{ha}$ ) has units of hectares. This can be converted to the area of the wetland in acres ( $A_A$ ) by dividing by 0.406. A land buffer for the wetland ( $B_W$ ) is generally used. The land buffer for the wetland is generally calculated at approximately 15% of the wetland area in acres ( $A_A$ ) and accounts for access points, berms and other features that require additional space. The total area of the wetland ( $A_W$ ) in acres is determined by the following equation:

$$A_W = (A_A)(B_W) \quad (8.9)$$

Another important feature to understand is the hydraulic retention time (HRT), in units of days, for the wetland. The HRT is used as a design check as constructed



wetlands generally require hydraulic retention times of not less than seven days to meet their design and treatment goals. The HRT is determined by the following equation:

$$\text{HRT} = [(A_{\text{ha}})(D_{\text{w}})(10,000)]/W_{\text{FR}} \quad (8.10)$$

where  $D_{\text{w}}$  is the average wetland design depth. The number 10,000 is the unit conversion between square meters and hectares ( $10,000\text{m}^2/\text{hectare}$ ).

The two primary fertilizer requirements are nitrogen and phosphorus. As demonstrated by this work and others, phosphorus is conserved in constructed wetlands. Therefore the phosphorus concentration coming out of the pretreatment step is generally the phosphorus concentration that will be found in the effluent of the constructed wetland system used for irrigation. The concentration of phosphorus is case specific and has to be assessed for each particular community considering a crop irrigation strategy. This is generally accomplished by looking at monthly or annual average total phosphorus concentration data for the wastewater plant conducting the feasibility analysis.

### ***8.3.0 Model Applications***

As discussed above, the model may be used for a wide range of population sizes and wastewater flow rates. In addition, the model may be used for a wide range of crops by varying the input assumptions for water and nutrient requirements. The following discussion demonstrates the utility of the model in determining the feasibility in two scenarios: 1) The City of Missoula, MT growing a winter canola crop, and 2) the Town of Culbertson, MT growing a spring canola crop.

### 8.3.1 City of Missoula – Winter Canola

The first question to be answered is the gallons of diesel fuel consumed per year ( $G_Y$ ) for the City of Missoula. This was assigned a value of 32,000 gallons per year through communication with the City of Missoula fleet manager.

The second question is the crop to be produced. A winter canola is the crop of choice for Missoula. Western Montana has an ideal climate for winter canola production. The relatively mild winters with valley snow cover provide suitable conditions for substantial and predictable yields. Winter canola is planted in the fall, generally emerges to a height of 3-5 inches with leaf production and root development prior to a frost or snow cover. Ideally no flower development occurs in the fall.



**Figure 85. Photo of winter canola crop in bloom at the Montana State University Western Agricultural Research Center in Creston, MT. Photo courtesy of Dr. Duane Johnson.**

The canola plant is then dormant over the winter months and, in general, if 30% of the plants survive with sufficient even spacing, then an economical crop can be realized. The canola will branch and fill in the void spaces generated by killed plants. The plant is most susceptible to being killed during the spring time when heaving may cause damage to roots when energy reserves are low. Windy conditions also desiccate exposed leaves putting additional stress on young root systems. Ideal conditions include a snow cover, which provides insulation over the winter that rapidly melts, followed by days of ideal growing conditions (102). While not discussed here, a significant body of knowledge exists on the production, harvesting, and storage of winter canola and an excellent starting point for more information can be found at [www.canolacouncil.org](http://www.canolacouncil.org).

The next step is to determine the acres necessary for production of the crop ( $A_c$ ). We start this analysis by understanding the potential yield per acre of crop ( $Y_c$ ) in pounds. For a winter canola under irrigation one can expect on the order of 4000 pounds of oilseed with oil content ( $O_c$ ) of approximately 40%. The oil must be extracted from the seed and it is assumed that this is done mechanically with an extraction efficiency ( $E_e$ ) of approximately 94%, meaning 94% of the oil available in the seed is recovered. Accounting for shrink ( $S$ ) of 2% the vegetable oil produced per acre of crop irrigated ( $O_p$ ) in Missoula is 1,473 pounds which can be converted to gallons by dividing by 7.8 as there are approximately 7.8 pounds of oil for every gallon of oil. The oil production is therefore approximately 188 gallons per acre. The conversion efficiency to fuel ( $F_c$ ) is approximately 95% meaning 95% of the oil produced is converted to a fuel equivalent methyl ester. Therefore, using Equation 8.1, approximately 180 gallons of diesel fuel is

produced per acre ( $F_p$ ). With this value, and using Equation 8.2, the model allows for the determination of  $A_c$  which, for Missoula, is approximately 178 acres.

The next step in the modeling process is to determine the daily irrigation requirements ( $I_D$ ) for the winter canola crop. Consulting references I determined that this crop will need approximately 20 acre-inches of water ( $W_{ain}$ ) over the course of its 180 day ( $D$ ) growing season. Knowing an  $A_c$  value of 178 acres I use Equation 8.3 to determine that the water requirements ( $W_g$ ) for the crop will be approximately 96 MM gallons. However, the model accounts for the local precipitation during the growing season ( $P_g$ ) for the acres of crop production which, for Missoula is approximately 35 MM gallons. The model also accounts for the irrigation efficiency using an irrigation efficiency coefficient ( $I_E$ ) and assuming we are using a center pivot irrigation system with today's efficiencies at approximately 90%. This provides for an  $I_E$  of 1.10 which accounts for 10% loss of water by the irrigation system. Finally, using these values and Equation 8.4, I determined  $I_D$  for Missoula to be approximately 375,668 gallons/day.

With the crop and irrigation requirements determined one can now focus on the nutrient requirements. Winter canola requires approximately 48 kg N/acre-year ( $N_R$ ) and 20.8 kg P/acre-year ( $P_R$ ). Focusing on the nitrogen requirements and using Equation 8.5, I determined the daily nitrogen requirements ( $N_D$ ) to be 47.54 kg/acre-day. Employing this value and Equation 8.6, I can now determine one of the most important values of the model, the nitrogen concentration requirement in the wetland effluent ( $N_{WE}$ ). For Missoula the  $N_{WE}$  is 33.41 mg/L.

The model is now used to determine the size of the wetland needed to meet the targeted  $N_{WE}$  and the targeted irrigation rate. This is a function of the flow rate through

the wetland and the concentration of nitrogen in the primary effluent.  $I_D$  is converted to cubic meters and determined to be 1422 m<sup>3</sup>/day. The  $ET_B$  coefficient is determined to be 1.15, and using Equation 8.7 one can calculate the wetland from rate ( $W_{FR}$ ) for Missoula to be 1635 m<sup>3</sup>/day (432,066 gallons of primary effluent must be added to the wetland per day). For the City of Missoula, the treatment before the constructed wetland is assumed to be a primary clarifier. The five year average total nitrogen ( $N_P$ ) concentration from the primary effluent was 60 mg/L. With this information the area of the wetland ( $W_{ha}$ ) can be determined with Equation 8.8. This value is 3.77 hectares, or approximately 9.30 acres. A buffer coefficient ( $B_W$ ) is utilized for berms and other wetland structures. Employing the buffer coefficient, I found the total size of the wetland system ( $A_W$ ) is 10.69 acres. Noting the design depth ( $D_W$ ) of 1 meter, I can compute the HRT using Equation 8.10. The HRT was determined to be approximately 23.1 days for the Missoula constructed wetland system.

### 8.3.2 Phosphorus and Salinity

The five-year average phosphorus concentration in the primary effluent at the Missoula wastewater treatment plant was 7.44 mg/L. This concentration is assumed to be conserved in the free water surface wetland treatment system that is modeled here. However, it is important to understand how much phosphorus winter canola needs and how much is provided at the given wetland effluent concentration. Winter canola requires 20.8 kg P/acre-season ( $P_R$ ). Knowing this the amount of phosphorus required per day ( $P_D$ ) can be determined by:

$$P_D = (P_R)(A_C)(1/D) \quad (8.11)$$

Using the value determined for  $P_D$ , I can determine the concentration of phosphorus needed in the wetland effluent by:

$$P_{WE} = (P_D)(1/I_D)(1,000,000\text{mg/kg})(0.264\text{gal/L}) \quad (8.12)$$

with  $P_{WE}$  having units of mg/L. For the winter canola  $P_{WE}$  is determined, using Equation 8.12, to be 14.44 mg/L. Noting the phosphorus is conserved in surface flow wetland systems and the influent concentration is 7.44 mg/L, I realize that additional phosphorus will have to be added to the irrigation water or provided by some other means to meet the winter canola crop demand.

Salinity can be assessed by looking at the electrical conductivity and the total dissolved solids (TDS) of the wetland effluent to be used for irrigation. Restrictions on the use of irrigation water with respect to salinity are presented in the table below.

|              | Degree of retriCTION on use |                    |        |       |
|--------------|-----------------------------|--------------------|--------|-------|
|              | None                        | Slight to Moderate | Severe |       |
| Salinity     |                             |                    |        | Units |
| Conductivity | 0.7                         | 0.7-3.0            | >3.0   | dS/m  |
| TDS          | <450                        | 450-2000           | >2000  | mg/L  |

**Table 33. Guidelines for salinity in irrigation water (38).**

From the data presented in section 10.0.0 a wetland system would only require no restrictions to slight restrictions over the course of the irrigation season for the crop.

### 8.3.3 Model Results for Missoula

Below is the feasibility model as generated from the assumptions entered into the spreadsheet. The light green boxes are numbers that the user must input into the model.



|   |                 |                        |                       |
|---|-----------------|------------------------|-----------------------|
| <b>Size of Wetland</b>  | <b>acres</b>    | <b>yds<sup>2</sup></b> | <b>ft<sup>2</sup></b> |
|   | 9.30            | 44,990                 | 134,969               |
| <b>Depth (yd)</b>   | <b>yd</b>       |                        |                       |
|   | 1.0936          |                        |                       |
| <b>Constuction Item<sup>1</sup></b>   | <b>Units</b>    | <b>Unit Price</b>      | <b>Total cost</b>     |
| Excavation/Compaction   | yd <sup>3</sup> | 1.5                    | \$ 73,801             |
| Soil  | yd <sup>3</sup> | 1.3079                 | \$ 6,435              |
| Gravel  | yd <sup>2</sup> | 13.079                 | \$ 58,842             |
| Liner   | yd <sup>2</sup> | 2.093                  | \$ 94,163             |
| Plants  | each            | 0.6                    | \$ 80,981             |
| Plumbing/Pumps <sup>2</sup>   | Lump Sum        |                        | \$ 7,500              |
| Control Stuctures   | Lump Sum        |                        | \$ 7,500              |
| Other   | Lump Sum        |                        | \$ 10,000             |
| Total Wetland Cost  |                 |                        | \$ 339,223            |
| <b>Irrigation Method</b>  |                 |                        |                       |
| Center Pivot  |                 | Yes                    |                       |
| Wheel Line  |                 | No                     |                       |
| Irrigation Equipment  | \$/acre         | \$ 700.00              | \$ 124,780            |
|   |                 |                        |                       |
| <b>Total System Cost</b>  |                 |                        | <b>\$ 464,003</b>     |
| <sup>1</sup> Derived from EPA Constucted Wetland Manual, 1999                               |                 |                        |                       |
| <sup>2</sup> Assumes preliminary treatment, pumping stations and collection system in place |                 |                        |                       |

**Table 35. Wetland and irrigation system estimated costs for Missoula.**

The wetland size and depth assumptions contribute to the system cost analysis. Here is a total wetland cost estimated at \$339,223. This assumes that all the preliminary treatment steps, collection system, and pumping system is in place. With Missoula it is assumed that a center pivot irrigation system will be used with an installed cost of \$124,780. The total wetland irrigation system cost is estimated at \$464,000.

The cost for the fuel must be determined as well. The following analysis includes costs for the seed, planting, harvesting and processing both the seed and oil into a suitable fuel. This assumes a small scale decentralized processing system is utilized for both extraction of the oil from the seed and processing of the oil into a suitable fuel. The cost of the oilseed processing equipment is not factored into this feasibility model. Labor costs are included with these assumptions. Below is a table showing the fuel production cost and savings for the City of Missoula.



| Crop Production and Fuel Cost Model |          |                   |              |
|-------------------------------------|----------|-------------------|--------------|
| Expense Item                        | Units    | Wetland Irrigated | Conventional |
| Seed                                | \$/acre  | \$ 30             | \$ 30        |
| Planting                            | \$/acre  | \$ 14             | \$ 14        |
| Harvesting                          | \$/acre  | \$ 26             | \$ 26        |
| Nitrogen                            | \$/acre  | \$ -              | \$ 36        |
| Phosphorus                          | \$/acre  | \$ -              | \$ 44        |
| Total Cost                          | \$/acre  | \$ 70             | \$ 150       |
| Yield/acre                          | lbs/acre | 4,000             | 4,000        |
| Oil Content                         | %        | 40%               | 40%          |
| lbs of seed/gallon                  | lbs/gal  | 19.50             | 19.50        |
| Cost of Seed                        | \$/lb    | \$ 0.0175         | \$ 0.0375    |
| Extraction Cost                     | \$/lb    | \$ 0.03           | \$ 0.02      |
| Cost of Oil                         | \$/gal   | \$ 0.84           | \$ 1.14      |
| Processing                          | \$/gal   | \$ 0.35           | \$ 0.25      |
| Shipping                            | \$/gal   | \$ 0.10           | \$ 0.25      |
| Fuel Cost Per Gal.                  | \$/gal   | \$ 1.29           | \$ 1.64      |
| Meal Credit                         | \$/lb    | \$ 0.54           | \$ 0.54      |
| Final Fuel Cost                     | \$/gal   | \$ 0.75           | \$ 1.10      |
| Total Fuel Cost                     | \$/year  | \$ 92,800.00      | \$ 92,800.00 |
| Annual Savings                      | \$/year  | \$ 68,760.00      | \$ 57,480.00 |

**Table 36. Fuel production costs and estimated savings for City of Missoula.**

The cost and simple return on investment summary is shown in the table below.

| Cost and Return on Investment (ROI) Summary |         |          |            |                                 |         |              |
|---|---------|----------|------------|---------------------------------|---------|--------------|
| Irrigation Method                           |         |          | Pivot      | Price of Diesel Fuel            | \$/gal  | \$ 2.90      |
| Cost of Irrigation Equipment Per Acre       | U.S. \$ | $I_{PA}$ | \$ 700.00  | Annual Fuel Costs               |         | \$ 92,800.00 |
| Cost of the Wetland                         | U.S. \$ | $C_w$    | \$ 339,223 | Irrigated Energy Crop Fuel Cost | \$/gal  | \$ 0.75      |
| Cost of Irrigation Equipment                | U.S. \$ | $I_C$    | \$ 124,780 | Annual Savings                  | \$/year | \$ 68,760.00 |
| Total Project Cost                          | U.S. \$ |          | \$ 464,003 | Simple ROI                      | years   | 6.75         |

**Table 37. Cost and simple return on investment for City of Missoula.**

These data presented in the table above indicate that the City of Missoula may realize an annual savings of approximately \$68,000 per year with a return on investment of approximately 6.75 years.

### 8.3.5 Conclusions for Missoula

The City of Missoula has sufficient wastewater for irrigation of the 178 acres of winter canola required to produce the 32,000 gallons of diesel fuel used annually by the City. The total cost of the 9.6 acre wetland system and 178 acres of irrigation under

center pivot was estimated to be approximately \$454,000. Using today's diesel fuel cost of approximately \$2.90/gallon, I calculated an annual fuel savings of \$68,760 assuming the City receives a road tax exemption on their diesel fuel use. A simple return on investment is calculated to be 6.75 years.

#### **8.4.0 Town of Culbertson Montana**

The town of Culbertson is located in northeastern Montana. It has a population of approximately 900 people with an annual average daily wastewater flow rate of approximately 125,000 gallons. Following the question and answer guidelines presented in section 11.2.0, I estimated that the town of Culbertson consumes approximately 1,500 gallons of diesel fuel per year. The oilseed crop suitable for Culbertson is a spring canola with a growing season of approximately 120 days. The crop, under irrigation, can be expected to yield on the average 2,000 pounds per acre and will require 20 acre inches (approximately 8.269 MM acre-gallons) of moisture over the course of its growing season. The natural precipitation is approximately 5 acre inches (approximately 2,000,000 acre-gallons). Nitrogen requirements are approximately 48 kg/acre-year for nitrogen and 20.8 kg/acre-year for phosphorus. The Town of Culbertson uses a facultative lagoon as their current treatment system. This is assumed to be replaced by a smaller constructed wetland system with an estimated influent nitrogen concentration of 60 mg/L and phosphorus concentration of 7.66 mg/L.

Entering these data into the feasibility model generated the results presented in the following table.



The total capital investment excluding land purchases is approximately \$76,000. This assumes the use of a wheel line for irrigation purposes. The return on investment for Culbertson, Montana is approximately 24 years with an annual fuel cost savings of \$3,136.88

#### **8.4.1 Culbertson, Montana Conclusions**

The model results suggest that, while feasible, the return on investment is very long. However, it is recommended that the maximum oilseed crop production potential be explored rather than just the amount of fuel the town consumes on an annual basis. The large tracts of farmland adjacent to the facility and the proximity of the community to a large oilseed crush operation provide additional economic advantages and feasibility to the community. By testing the model limits in terms of the total amount of wastewater available for irrigation on an average basis, the Town of Culbertson could reasonably irrigate 28 acres of crop using 108,000 gallons of wastewater for the production of 2800 gallons of fuel per year. The summary of this analysis is provided below.

| Irrigated Energy Crop - Winter Canola    |              |           |            | Fuel Production Model         |              |        |             |
|--|--------------|-----------|------------|-------------------------------|--------------|--------|-------------|
| Assumptions                              | Units        | Symbol    | Value      | Variable                      | Units        | Symbol | Value       |
| Municipality Requirements                |              |           |            | Yield of Seed Per Acre        | lbs/acre     | $Y_c$  | 2,000       |
| Diesel Fuel Use                          | gallons/year | $G_y$     | 2,800      | Oil Content                   | %            | $O_c$  | 40%         |
| Wastewater Characteristics (Summer)      |              |           |            | Extraction Efficiency         | %            | $E_e$  | 99%         |
| Primary Effluent Nitrogen Concentration  | mg/L         | $N_p$     | 60         | Shrink                        | %            | $S$    | 1%          |
| Primary Effluent Phosphorus Conc.        | mg/L         | $P_p$     | 7.66       | Oil Produced per acre         | lbs/acre     | $O_p$  | 784.08      |
| Crop Requirements                        |              |           |            | Pounds of oil per gallon      | lbs/gallon   |        | 7.80        |
| Growing Season                           | Days         | $D$       | 120        | Oil Produced per acre         | gallons/acre | $O_o$  | 100.5230769 |
| Fertilizer                               |              |           |            | Conversion to Fuel Efficiency |              | $F_c$  | 98%         |
| Nitrogen                                 | kg/acre-year | $N_R$     | 48         | Fuel Produced Per Acre        | gallons/acre | $F_p$  | 99          |
| Phosphorus                               | kg/acre-year | $P_R$     | 20.8       | Diesel Fuel Use               | gallons      | $G_D$  | 2,800       |
| Water                                    |              |           |            | Crop Land Needed              | acres        | $A_c$  | 28          |
| Total Water Requirements                 | ac/in        | $W_{ain}$ | 20         | Total Fuel Production         | gallons      | $F_T$  | 2,800       |
| Total Water Requirements                 | acre/gallons | $W_{ag}$  | 15,435,830 |                               |              |        |             |
| Natural Precipitation                    |              |           |            |                               |              |        |             |
| Acre Inches (Avg Growing Season)         | acre/in      | $P_{ain}$ | 5          |                               |              |        |             |
| Acre Gallons                             | acre/gallons | $P_{ag}$  | 3,858,958  |                               |              |        |             |
| Estimated Crop Production                |              |           |            |                               |              |        |             |
| Estimated Yield of Seed per acre         | lbs/acre     | $Y_c$     | 2,000      |                               |              |        |             |
| Oil Content                              | %            | $O_c$     | 40%        |                               |              |        |             |
| <b>Results</b>                           |              |           |            |                               |              |        |             |
| Irrigation Requirements                  |              |           |            |                               |              |        |             |
| Acre inches                              | ac/in        | $I_{ain}$ | 15         |                               |              |        |             |
| Gallons                                  | gallons      | $I_g$     | 11,576,873 |                               |              |        |             |
| Irrigation Efficiency                    |              | $I_E$     | 1.10       |                               |              |        |             |
| Daily Irrigation Requirements            | gallons/day  | $I_D$     | 106,121    |                               |              |        |             |
| Fuel Produced                            | gallons      | $F_P$     | 2,800      |                               |              |        |             |
| Crop Land needed for fuel production     | acres        | $A_c$     | 28         |                               |              |        |             |
| Size of Wetland System                   | acres        | $A_w$     | 3.02       |                               |              |        |             |
| Total Land Requirements                  | acres        | $L_T$     | 31.44      |                               |              |        |             |
| Depth                                    | ft           | $D_W$     | 3.2808     |                               |              |        |             |
| Volume of Primary Effluent Added Per Day | gallons/day  | $E_g$     | 122,053    |                               |              |        |             |

**Table 40. Maximum wetland irrigation system size for Culbertson, Montana.**

As demonstrated by these data presented in the table below, the simple return on investment at current fuel price levels is approximately 20 years.

| Cost and Return on Investment (ROI) Summary |         |            |            |                                 |         |             |
|---|---------|------------|------------|---------------------------------|---------|-------------|
| Irrigation Method                           |         | Wheel Line |            | Price of Diesel Fuel            | \$/gal  | \$ 2.90     |
| Cost of Irrigation Equipment Per Acre       | U.S. \$ | $I_{PA}$   | \$ 250.00  | Annual Fuel Costs               |         | \$ 8,120.00 |
| Cost of the Wetland                         | U.S. \$ | $C_w$      | \$ 113,764 | Irrigated Energy Crop Fuel Cost | \$/gal  | \$ 0.81     |
| Cost of Irrigation Equipment                | U.S. \$ | $I_C$      | \$ 7,106   | Annual Savings                  | \$/year | \$ 5,855.50 |
| Total Project Cost                          | U.S. \$ |            | \$ 120,869 | Simple ROI                      | years   | 20.64       |

**Table 41. Cost and simple return on investment for maximum irrigation in Culbertson.**

### 8.5.0 Irrigation Model Conclusions

The model provides a simple feasibility tool by which a municipality may understand the potential to either grow an energy crop for its own use or as a revenue stream through the sale of the crop for further processing. The model does not address the nuances associated with specific municipalities, in particular land costs, public perception, or other intangibles that are unique to individual towns or cities. There is

evidence that limitations exist in terms of the size of communities most appropriate for the type of wastewater reuse that this model applies to. As represented in the two examples above, the City of Missoula, MT has sufficient wastewater for irrigation to supply all of its diesel fuel needs and has a relatively short payback appropriate for the public sector but struggles with land values and land constraints, whereas smaller rural communities, such as Culbertson, MT have limited wastewater flow rates for irrigation of an energy crop but have ample land resources and existing processing infrastructure nearby. Ultimately this model can be used as a tool to assess the feasibility prior to committing to additional development and preliminary engineering and permit costs.

The model was utilized to generate a series of simple mathematical relationships. The first one is the gallons of diesel fuel that a community uses as this relates to the required size of the constructed wetland. This is represented by the equation below.

$$A_W = 0.0002G_Y - 0.0013 \quad (8.13)$$

In addition, the relation between the crop land necessary and the amount of diesel fuel consumed by a municipality is shown below.

$$A_C = 0.0056G_Y - 0.079 \quad (8.14)$$

Finally, the relationship between the volume of wastewater required with respect to the diesel fuel consumed by a municipality is provided below.

$$E_g = 12.273G_Y \quad (8.15)$$

Each of these equations assumes 60 mg/L of TN and 7 mg/L of TP in the wastewater entering the wetland treatment systems. While these relationships provide for a rapid assessment of wetland size, cropland, and volume of primary effluent, for communities

with other nitrogen and phosphorus concentrations in their primary wastewater, it is necessary to input the additional information into the model to determine feasibility.

## 9.0.0 Conclusions

Focusing first on the City of Missoula, this work suggests that total treatment of all the municipal wastewater produced in Missoula with constructed wetlands is not feasible. This is primarily due to the land constraints, related costs to benefits and as these related to performance variability found and overall lack of this experimental scale wetland to achieve permissible limits of effluent discharge. The results of this work did suggest that partial treatment of a portion of the final or primary effluent in a smaller scale wetland treatment system is possible and is worthy of additional investigation. This approach would possibly consist of a constructed wetland system integrated into the current biological nutrient removal treatment process. This integrated constructed wetland treatment system may provide a buffer for treatment capacity whereby the wastewater treatment operations could use the constructed wetland system during times of process disruption. In practice, rather than discharging to the Clark Fork, effluent could be discharged to the wetland treatment system during events when treatment plant effluent is exceeding permissible limits.

This work has discovered that there are a number of options for the treatment plant at the City of Missoula to incorporate constructed wetlands and other constructed natural systems into the existing treatment scheme. It is concluded that no single natural treatment system operating alone will provide the necessary treatment required to sustain permitted discharge limits. If the City of Missoula determines that a natural treatment system is the direction it wishes to take, it is recommended that a combination of alternative treatment options be investigated and employed to reduce the nutrient impact on the Clark Fork River or for potential economic value. This combination could



possibly include a free water surface wetland and an integrated system of hybrid poplars and potential crop irrigation or other land application methodologies.

In summary, constructed wetlands are not viable options for total treatment of all the wastewater generated by the City of Missoula. However, properly scaled, constructed wetlands may provide services to the treatment plant in terms of 1) periodic additional capacity, 2) aesthetic and education outreach, 3) as a local source of information and demonstration through which surrounding rural communities in the Clark Fork River watershed and beyond may understand the practical merits of wetland treatment systems for their particular community.

This work investigated the seasonal treatment performance using primary effluent and an experimental scale constructed wetland. The treatment of pollutants and nutrients in this constructed wetland was challenging regardless of the season. By far the spring and the fall seasons present the most favorable ambient environmental conditions for the treatment of municipal wastewater in a constructed wetland. Intuition would suggest that the summertime season would provide ideal conditions. This work concluded that the summertime has limitations related to the build up and subsequent concentration of pollutants and nutrients. The primary issues with summertime treatment performance are biomass production within the system coupled with evapotranspiration.

Evapotranspiration, the combined evaporation and uptake of water by plants, reduces the volume of water in the wetland system over the course of the treatment cycle. This reduction in water volume causes the concentration of pollutants to increase in any particular sample. The large amount of sunshine and nutrient rich environment creates ideal conditions for biomass production. This biomass production can be related to the

nitrification process whereby 0.131 g of biomass are created for every 1 g of  $\text{NH}_4^+$  nitrified. This production of biomass contributes to TSS and BOD concentrations and the cell tissues, through ammonification, contribute to additional  $\text{NH}_4^+$ . This “feedback” loop within the system primarily found during the summer season, places additional stress on the ability of the wetland meet permissible discharge guidelines.

The discharge permit for municipalities does not change with the seasons. Evaluating the seasonal data with respect to these discharge permits, as provided in Table 30 above, this work concludes that BOD and TSS 30 day permit limits are achievable irrespective of the season, whereas the wetland violates TN permit limits in each season. In addition, this experimental system was unable to reduce the concentration of total phosphorus within any season or singular treatment cycle. As the data in table 31 demonstrate, BOD and TSS performance is quite good with respect to the permit limit whereas the TN permit limit is violated in each of the four seasons. This work concluded that overall the autumn season presents the best ambient seasonal conditions for relying on a constructed wetland to provide treatment of municipal wastewater.

Prior work has concluded that wetland nutrients and pollutants follow first order chemical kinetics. This work investigated this conclusion and compared zero, first and second order kinetics with certain seasonal data. COD, TSS,  $\text{NH}_4^+$  and TKN kinetics were investigated. Rate constants ( $k^{-1}$  in units of  $\text{hrs}^{-1}$ ) and a regression analysis comparison were conducted for each of the kinetic orders. The actual data did not follow the modeled kinetic data at later sample times. Therefore two regression analyses were conducted, one with all the data and one with the outlier removed. A total of 32 comparisons were made. A comparison of the  $r^2$  values suggest that second order

kinetics more accurately describes the chemistry of a constructed wetland treatment system 69% of the time with zero order at 22% and first order at 9%. Focusing on the data with out the outliers removed, second order kinetics was found 75% of the time with zero and first at 19% and 6% respectively. With the outlier removed the data suggested second order kinetics 63% of the time with zero and first at 25% and 13% respectively. Seasonally, second order kinetics more accurately described the treatment in Fall, Winter and Summer. Spring was a mix of second and zero order kinetics. *In conclusion, there appears to be, and as this kinetic investigation suggests, much deeper chemical dynamics that are at play within wetland treatment systems and this simple whole order analysis does not provide any definitive conclusions on the actual chemical kinetics occurring within the experimental wetland system.*

Knowing that pollutants are managed by wetland treatment systems, the question presents itself as to what value can be realized from the remaining nutrients found in wastewater. Reuse of this wastewater was investigated. This work concluded that pollutant management by a constructed wetland treatment system with subsequent reuse of nutrient rich wetland effluent in crop irrigation applications is possible. In particular, this work concluded that irrigation of an industrial oilseed crop with subsequent harvesting and processing of the oilseed to produce a fuel grade vegetable oil for use by the municipality. Furthermore, this work attempted to draw a mathematical relationship between a municipalities liquid fuel needs and the size of a wetland treatment system. As a way to test the model, it was applied to the City of Missoula. It was concluded that the City of Missoula has sufficient wastewater for irrigation of approximately 178 acres of winter canola required to produce the 32,000 gallons of diesel fuel used annually by the

City. The total cost of the 9.6 acre wetland system and 178 acres of irrigation under center pivot was estimated to be approximately \$454,000. Using today's diesel fuel cost of approximately \$2.90/gallon, the annual fuel savings realized are \$68,760 assuming the City receives a road tax exemption on their diesel fuel use. A simple return on investment was calculated to be 6.75 years.

The model provides a simple feasibility tool by which a municipality may understand the potential to either grow an energy crop for its own use or as a revenue stream through the sale of the crop for further processing. The model does not address the nuances associated with specific municipalities, in particular land costs, public perception, or other intangibles that are unique to individual towns or cities. There is evidence that limitations exist in terms of the size of communities most appropriate for the type of wastewater reuse that this model applies to. As concluded from the two communities to which the model was applied, the City of Missoula, MT has sufficient wastewater for irrigation to supply all of its diesel fuel needs and has a relatively short payback appropriate for the public sector but struggles with land values and land constraints. Smaller rural communities, such as Culbertson, MT have limited wastewater flow rates for irrigation of an energy crop but have ample land resources and existing processing infrastructure nearby. Ultimately, this model can be used as a tool to assess the feasibility prior to committing to additional development and preliminary engineering and permit costs.

The model was utilized to generate a series of simple mathematical relationships. The first one (equation 13 above) is the gallons of diesel fuel that a community uses as this relates to the requisite size of the constructed wetland. In addition, the relation

between the crop land necessary and the amount of diesel fuel consumed by a municipality is provided by equation 14. Finally, the relationship between the volume of wastewater required with respect to the diesel fuel consumed by a municipality is provided by Equation 8.15. Each of these equations assumes 60 mg/L of TN and 7 mg/L of TP in the wastewater entering the wetland treatment systems. While these relationships provide for a rapid assessment of wetland size, cropland, and volume of primary effluent, for communities with other nitrogen and phosphorus concentrations in their primary effluent, it is necessary to input the additional information into the model to determine feasibility.

Our society has been conditioned to regard wastewater by its namesake as “waste”. It is true that there are pollutants within this water stream that need to be addressed and can be addressed and managed by natural systems. As we journey into the 21<sup>st</sup> century and resources become constrained our society may need to reconsider the beneficial features and more importantly the potential energy found in the nutrients within this municipal or better yet, urban resource.



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# 11.0.0 Appendix

## A. Historical Primary effluent data

| Historical Data for Primary effluent at the City of Missoula Waste Water Treatment Plant (WWTP) Data year starts in January of 1999 and ends in April of 2003. |            |             |            |            |            |            |           |            |           |           |            |           |            |
|--|------------|-------------|------------|------------|------------|------------|-----------|------------|-----------|-----------|------------|-----------|------------|
| Date   | PrimaryNH3 | Date        | PrimaryTKN | Date       | PrimaryNO3 | Date       | PrimaryTP | Date       | PrimarySP | Date      | PrimaryTSS | Date      | PrimaryBOD |
| 1/8/1999   | 26.21      | 1/8/1999    | 36.54      | 1/8/1999   | 0.11       | 1/8/1999   | 7.92      | 1/8/1999   | 6.17      | 1/1/1999  | 93         | 1/1/1999  | 150        |
| 1/15/1999  | 23.68      | 1/14/1999   | 29.29      | 1/15/1999  | 0.02       | 1/14/1999  | 7.17      | 1/14/1999  | 5.60      | 1/4/1999  | 85         | 1/4/1999  | 172.5      |
| 1/20/1999  | 22.91      | 1/21/1999   | 24.33      | 1/20/1999  | 0.84       | 2/5/1999   | 6.78      | 1/21/1999  | 4.64      | 1/5/1999  | 75         | 1/5/1999  | 135        |
| 1/29/1999  | 23.63      | 1/27/1999   | 26.86      | 1/29/1999  | 1.10       | 2/11/1999  | 6.40      | 2/5/1999   | 4.90      | 1/6/1999  | 73         | 1/6/1999  | 165        |
| 2/2/1999   | 18.39      | 2/5/1999    | 28.52      | 2/2/1999   | 1.16       | 2/18/1999  | 7.85      | 2/11/1999  | 4.22      | 1/7/1999  | 78         | 1/7/1999  | 157.5      |
| 2/12/1999  | 22.07      | 2/11/1999   | 30.13      | 2/12/1999  | 1.43       | 3/4/1999   | 8.19      | 2/18/1999  | 5.19      | 1/21/1999 | 81         | 1/8/1999  | 125        |
| 2/18/1999  | 19.35      | 3/4/1999    | 27.33      | 2/18/1999  | 0.92       | 3/11/1999  | 7.47      | 2/24/1999  | 5.25      | 1/11/1999 | 85         | 1/11/1999 | 260        |
| 2/23/1999  | 19.52      | 3/11/1999   | 27.47      | 2/23/1999  | 1.25       | 3/19/1999  | 8.05      | 3/4/1999   | 5.75      | 1/12/1999 | 82         | 1/12/1999 | 170        |
| 3/3/1999   | 21.02      | 3/19/1999   | 25.70      | 3/3/1999   | 1.25       | 3/26/1999  | 6.65      | 3/11/1999  | 5.30      | 1/13/1999 | 76         | 1/13/1999 | 170        |
| 3/12/1999  | 22.52      | 3/26/1999   | 23.31      | 3/12/1999  | 0.88       | 3/31/1999  | 7.28      | 3/19/1999  | 2.32      | 1/14/1999 | 93         | 1/14/1999 | 245        |
| 3/16/1999  | 23.17      | 3/31/1999   | 23.31      | 3/16/1999  | 1.09       | 4/8/1999   | 7.55      | 3/26/1999  | 4.66      | 1/15/1999 | 84         | 1/15/1999 | 200        |
| 3/25/1999  | 18.08      | 4/8/1999    | 29.52      | 3/25/1999  | 1.26       | 4/15/1999  | 7.54      | 4/8/1999   | 5.13      | 1/18/1999 | 90         | 1/18/1999 | 360        |
| 4/6/1999   | 17.78      | 4/15/1999   | 28.84      | 3/31/1999  | 1.44       | 4/23/1999  | 8.51      | 4/15/1999  | 4.53      | 1/19/1999 | 92         | 1/19/1999 | 180        |
| 4/15/1999  | 22.64      | 4/23/1999   | 27.63      | 4/6/1999   | 0.71       | 4/28/1999  | 9.72      | 4/23/1999  | 6.29      | 1/20/1999 | 80         | 1/20/1999 | 310        |
| 4/22/1999  | 20.95      | 4/28/1999   | 35.23      | 4/22/1999  | 0.55       | 5/7/1999   | 10.10     | 4/28/1999  | 6.26      | 1/21/1999 | 90         | 1/21/1999 | 165        |
| 4/28/1999  | 25.52      | 5/7/1999    | 34.95      | 4/28/1999  | 0.00       | 5/12/1999  | 9.63      | 5/7/1999   | 6.81      | 1/22/1999 | 90         | 1/22/1999 | 190        |
| 5/6/1999   | 27.08      | 5/12/1999   | 34.05      | 5/6/1999   | 0.00       | 5/20/1999  | 9.23      | 5/12/1999  | 6.54      | 1/25/1999 | 97         | 1/25/1999 | 142.5      |
| 5/10/1999  | 25.26      | 5/20/1999   | 31.03      | 5/10/1999  | 0.00       | 5/28/1999  | 7.59      | 5/20/1999  | 6.96      | 1/26/1999 | 89         | 1/26/1999 | 230        |
| 5/18/1999  | 23.81      | 5/28/1999   | 24.64      | 5/18/1999  | 0.00       | 6/3/1999   | 6.90      | 5/28/1999  | 5.49      | 1/27/1999 | 91         | 1/27/1999 | 150        |
| 5/27/1999  | 16.65      | 6/3/1999    | 21.98      | 5/27/1999  | 1.34       | 6/11/1999  | 6.78      | 6/3/1999   | 4.60      | 1/28/1999 | 80         | 1/28/1999 | 232.5      |
| 6/3/1999   | 15.1       | 6/11/1999   | 22.57      | 6/3/1999   | 0.04       | 6/17/1999  | 7.82      | 6/11/1999  | 4.70      | 1/29/1999 | 83         | 1/29/1999 | 175        |
| 6/10/1999  | 18.86      | 6/17/1999   | 24.36      | 6/10/1999  | 0.00       | 6/25/1999  | 8.36      | 6/17/1999  | 5.71      | 2/1/1999  | 101        | 2/1/1999  | 272.5      |
| 6/16/1999  | 16.28      | 6/25/1999   | 23.35      | 6/16/1999  | 0.04       | 7/1/1999   | 7.59      | 6/25/1999  | 6.42      | 2/2/1999  | 114        | 2/2/1999  | 215        |
| 6/21/1999  | 17.79      | 7/1/1999    | 31.41      | 6/21/1999  | 0.13       | 7/9/1999   | 8.12      | 7/1/1999   | 5.94      | 2/3/1999  | 106        | 2/3/1999  | 167.5      |
| 6/29/1999  | 15.26      | 7/9/1999    | 33.43      | 7/9/1999   | 0.00       | 7/15/1999  | 7.92      | 7/9/1999   | 6.28      | 2/4/1999  | 107        | 2/4/1999  | 210        |
| 7/9/1999   | 20.98      | 7/15/1999   | 32.77      | 7/13/1999  | 0.00       | 7/22/1999  | 7.29      | 7/15/1999  | 6.10      | 2/5/1999  | 110        | 2/5/1999  | 170        |
| 7/13/1999  | 15.15      | 7/22/1999   | 30.69      | 7/22/1999  | 0.00       | 7/30/1999  | 6.94      | 7/22/1999  | 5.47      | 2/8/1999  | 97         | 2/8/1999  | 287.5      |
| 7/22/1999  | 20.5       | 7/30/1999   | 27.58      | 7/26/1999  | 0.00       | 8/13/1999  | 7.61      | 7/30/1999  | 5.59      | 2/9/1999  | 129        | 2/9/1999  | 185        |
| 7/26/1999  | 18.32      | 8/13/1999   | 33.26      | 8/13/1999  | 0.00       | 8/20/1999  | 8.04      | 8/13/1999  | 4.88      | 2/10/1999 | 116        | 2/10/1999 | 215        |
| 8/13/1999  | 23         | 8/20/1999   | 30.31      | 8/20/1999  | 0.00       | 8/27/1999  | 7.62      | 8/20/1999  | 5.80      | 2/11/1999 | 117        | 2/11/1999 | 177.5      |
| 8/20/1999  | 19.68      | 8/27/1999   | 28.16      | 8/20/1999  | 1.68       | 9/3/1999   | 7.83      | 9/3/1999   | 5.50      | 2/12/1999 | 100        | 2/12/1999 | 190        |
| 8/26/1999  | 21.34      | 9/3/1999    | 36.99      | 9/3/1999   | 0.00       | 9/10/1999  | 7.83      | 9/10/1999  | 5.79      | 2/15/1999 | 128        | 2/15/1999 | 128        |
| 9/3/1999   | 25.89      | 9/10/1999   | 36.77      | 9/8/1999   | 0.00       | 9/17/1999  | 6.21      | 9/17/1999  | 3.96      | 2/16/1999 | 116        | 2/16/1999 | 145        |
| 9/8/1999   | 29.14      | 9/17/1999   | 32.87      | 9/15/1999  | 0.46       | 9/24/1999  | 6.28      | 9/24/1999  | 4.37      | 2/17/1999 | 121        | 2/17/1999 | 220        |
| 9/15/1999  | 20.16      | 9/24/1999   | 32.36      | 9/21/1999  | 0.34       | 9/30/1999  | 6.82      | 9/30/1999  | 4.88      | 2/18/1999 | 137        | 2/18/1999 | 147.5      |
| 9/21/1999  | 18.83      | 9/30/2/1999 | 35.16      | 9/29/1999  | 1.24       | 10/8/1999  | 8.28      | 10/8/1999  | 5.83      | 2/19/1999 | 99         | 2/19/1999 | 150        |
| 9/29/1999  | 21.26      | 10/8/1999   | 33.75      | 10/8/1999  | 3.57       | 10/15/1999 | 9.80      | 10/15/1999 | 6.91      | 2/22/1999 | 149        | 2/22/1999 | 190        |
| 10/6/1999  | 20.9       | 10/15/1999  | 38.74      | 10/12/1999 | 0.05       | 10/21/1999 | 9.79      | 10/21/1999 | 6.99      | 2/23/1999 | 126        | 2/23/1999 | 185        |
| 10/12/1999   | 27.97      | 10/21/1999  | 38.96      | 10/22/1999 | 0.05       | 10/29/1999 | 7.68      | 10/29/1999 | 5.21      | 2/24/1999 | 140        | 2/24/1999 | 210        |
| 10/22/1999   | 28.92      | 10/29/1999  | 34.38      | 10/29/1999 | 0.05       | 11/4/1999  | 7.65      | 11/4/1999  | 5.44      | 2/25/1999 | 147        | 2/25/1999 | 177.5      |
| 11/3/1999  | 23.94      | 11/4/1999   | 34.50      | 11/3/1999  | 0.08       | 11/12/1999 | 7.72      | 11/12/1999 | 4.52      | 2/26/1999 | 122        | 2/26/1999 | 130        |
| 11/19/1999   | 30.09      | 11/12/1999  | 36.37      | 11/19/1999 | 0.02       | 11/17/1999 | 10.19     | 11/17/1999 | 7.18      | 3/1/1999  | 140        | 3/1/1999  | 132.5      |
| 11/23/1999   | 26.19      | 11/17/1999  | 39.67      | 11/23/1999 | 0.18       | 11/26/1999 | 8.30      | 11/26/1999 | 6.01      | 3/2/1999  | 131        | 3/2/1999  | 140        |
| 12/1/1999  | 22.8       | 11/26/1999  | 29.88      | 11/26/1999 | 0.02       | 12/2/1999  | 9.51      | 12/2/1999  | 6.76      | 3/3/1999  | 109        | 3/3/1999  | 167.5      |
| 1/28/1999  | 24.01      | 12/2/1999   | 37.22      | 12/1/1999  | 0.94       | 12/10/1999 | 8.13      | 12/10/1999 | 5.97      | 3/4/1999  | 110        | 3/4/1999  | 187.5      |
| 1/27/1999  | 23.6       | 12/10/1999  | 33.91      | 12/23/1999 | 1.77       | 12/17/1999 | 8.62      | 12/17/1999 | 6.44      | 3/5/1999  | 107        | 3/5/1999  | 217.5      |
| 1/23/1999  | 21.13      | 12/17/1999  | 34.43      | 12/28/1999 | 1.43       | 12/23/1999 | 8.42      | 1/14/2000  | 5.98      | 3/8/1999  | 85         | 3/8/1999  | 140        |
| 1/28/1999  | 22.81      | 12/23/1999  | 35.33      | 1/6/2000   | 0.02       | 12/29/1999 | 8.28      | 12/12/2000 | 5.48      | 3/9/1999  | 87         | 3/9/1999  | 135        |
| 1/6/2000   | 23.46      | 12/29/1999  | 30.81      | 1/14/2000  | 0.02       | 12/23/1999 | 6.09      | 1/26/2000  | 5.97      | 3/10/1999 | 79         | 3/10/1999 | 182.5      |
| 1/14/2000  | 25.79      | 1/7/2000    | 39.66      | 1/7/2000   | 9.26       | 12/29/1999 | 5.95      | 2/4/2000   | 5.20      | 3/11/1999 | 88         | 3/11/1999 | 150        |
| 1/21/2000  | 24.58      | 1/14/2000   | 39.98      | 1/14/2000  | 8.54       | 1/7/2000   | 6.92      | 2/10/2000  | 5.27      | 3/12/1999 | 86         | 3/12/1999 | 130        |
| 1/25/2000  | 27.17      | 1/21/2000   | 40.48      | 2/2/2000   | 0.88       | 1/21/2000  | 7.98      | 2/17/2000  | 5.38      | 3/15/1999 | 94         | 3/15/1999 | 192.5      |
| 2/2/2000   | 20.02      | 1/26/2000   | 42.25      | 2/8/2000   | 0.04       | 1/26/2000  | 8.11      | 2/24/2000  | 5.38      | 3/16/1999 | 88         | 3/16/1999 | 127.5      |
| 2/9/2000   | 27.61      | 2/4/2000    | 35.40      | 2/15/2000  | 0.02       | 2/4/2000   | 8.95      | 3/3/2000   | 5.10      | 3/17/1999 | 85         | 3/17/1999 | 135        |
| 2/15/2000  | 25.58      | 2/10/2000   | 31.02      | 2/10/2000  | 0.02       | 2/10/2000  | 7.98      | 3/10/2000  | 5.72      | 3/18/1999 | 83         | 3/18/1999 | 145        |
| 2/24/2000  | 25.43      | 2/17/2000   | 37.01      | 3/1/2000   | 0.36       | 2/17/2000  | 7.89      | 3/17/2000  | 5.17      | 3/19/1999 | 76         | 3/19/1999 | 155        |
| 3/1/2000   | 21.34      | 2/24/2000   | 37.80      | 3/8/2000   | 0.04       | 2/24/2000  | 8.60      | 3/23/2000  | 5.44      | 3/22/1999 | 61         | 3/22/1999 | 152.5      |
| 3/8/2000   | 28.32      | 3/3/2000    | 39.18      | 4/7/2000   | 0.05       | 3/3/2000   | 7.74      | 3/31/2000  | 5.32      | 3/23/1999 | 90         | 3/23/1999 | 155        |
| 4/7/2000   | 25.7       | 3/10/2000   | 39.25      | 4/12/2000  | 0.02       | 3/10/2000  | 8.18      | 4/6/2000   | 5.98      | 3/24/1999 | 95         | 3/24/1999 | 175        |
| 4/12/2000  | 24.28      | 3/17/2000   | 37.22      | 4/18/2000  | 0.02       | 3/17/2000  | 8.03      | 4/21/2000  | 4.78      | 3/25/1999 | 98         | 3/25/1999 | 145        |
| 4/18/2000  | 28.14      | 3/23/2000   | 34.70      | 4/24/2000  | 0.02       | 3/23/2000  | 8.28      | 4/27/2000  | 5.01      | 3/26/1999 | 117        | 3/26/1999 | 142.5      |
| 4/24/2000  | 23.75      | 3/31/2000   | 34.39      | 5/2/2000   | 0.03       | 3/31/2000  | 7.86      | 5/5/2000   | 5.40      | 3/29/1999 | 99         | 3/29/1999 | 167.5      |
| 5/2/2000   | 23.3       | 4/6/2000    | 38.24      | 5/10/2000  | 0.03       | 4/6/2000   | 8.33      | 5/11/2000  | 5.86      | 3/30/1999 | 98         | 3/30/1999 | 137.5      |
| 5/8/2000   | 27.45      | 4/21/2000   | 36.22      | 5/19/2000  | 0.04       | 4/21/2000  | 6.88      | 5/19/2000  | 5.79      | 3/31/1999 | 92         | 3/31/1999 | 165        |
| 5/19/2000  | 22.95      | 4/27/2000   | 35.66      | 5/23/2000  | 0.04       | 4/27/2000  | 7.57      | 5/26/2000  | 5.69      | 4/5/1999  | 113        | 4/1/1999  | 125        |
| 5/23/2000  | 25.25      | 5/5/2000    | 33.91      | 5/30/2000  | 0.03       | 5/5/2000   | 7.88      | 5/31/2000  | 5.15      | 4/7/1999  | 96         | 4/5/1999  | 170        |
| 5/30/2000  | 21.73      | 5/11/2000   | 35.91      | 6/6/2000   | 0.03       | 5/11/2000  | 8.29      | 6/15/2000  | 4.49      | 4/8/1999  | 89         | 4/6/1999  | 160        |
| 6/5/2000   | 18.25      | 5/19/2000   | 34.04      | 6/14/2000  | 0.04       | 5/19/2000  | 7.63      | 6/23/2000  | 4.69      | 4/9/1999  | 85         | 4/7/1999  | 222.5      |
| 6/14/2000  | 24.37      | 5/25/2000   | 33.67      | 6/19/2000  | 0.03       | 5/26/2000  | 7.69      | 6/28/2000  | 4.48      | 4/12/1999 | 91         | 4/8/1999  | 120        |
| 6/19/2000  | 25.05      | 5/31/2000   | 35.17      | 6/28/2000  | 0.02       | 5/31/2000  | 7.55      | 7/6/2000   | 4.69      | 4/13/1999 | 86         | 4/9/1999  | 135        |
| 6/28/2000  | 25.1       | 6/15/2000   | 36.25      | 7/7/2000   | 0.01       | 6/15/2000  | 7.06      | 7/14/2000  | 4.82      | 4/14/1999 | 91         | 4/12/1999 | 130        |
| 7/3/2000   | 23.22      | 6/23/2000   | 33.37      | 7/11/2000  | 0.02       | 6/23/2000  | 7.02      | 7/21/2000  | 5.32      | 4/15/1999 | 93         | 4/13/1999 | 90         |
| 7/11/2000  | 24.85      | 6/28/2000   | 33.61      | 7/18/2000  | 0.03       | 6/28/2000  | 6.46      | 7/28/2000  | 5.36      | 4/16/1999 | 103        | 4/14/1999 | 115        |
| 7/18/2000  | 27.26      | 7/14/2000   | 36.72      | 7/24/2000  |            |            |           |            |           |           |            |           |            |

|            |       |            |       |            |       |            |       |            |      |           |     |           |       |
|------------|-------|------------|-------|------------|-------|------------|-------|------------|------|-----------|-----|-----------|-------|
| 1/3/2001   | 25.57 | 1/5/2001   | 39.49 | 1/8/2001   | 0.01  | 12/28/2000 | 9.34  | 1/19/2001  | 6.49 | 6/3/1999  | 106 | 5/25/1999 | 115   |
| 1/8/2001   | 23.3  | 1/12/2001  | 38.53 | 1/16/2001  | 0.02  | 1/16/2001  | 7.41  | 1/26/2001  | 6.68 | 6/4/1999  | 99  | 5/26/1999 | 150   |
| 1/16/2001  | 23.97 | 1/19/2001  | 39.87 | 1/24/2001  | 0.01  | 1/12/2001  | 8.84  | 1/31/2001  | 7.22 | 6/7/1999  | 72  | 5/27/1999 | 90    |
| 1/24/2001  | 27.99 | 1/26/2001  | 39.51 | 2/13/2001  | 0.17  | 1/19/2001  | 8.83  | 2/9/2001   | 9.49 | 6/8/1999  | 86  | 5/28/1999 | 142.5 |
| 1/29/2001  | 26.31 | 1/31/2001  | 38.99 | 2/21/2001  | 0.39  | 1/26/2001  | 9.12  | 2/16/2001  | 8.03 | 6/10/1999 | 74  | 5/31/1999 |       |
| 2/5/2001   | 27.45 | 2/9/2001   | 41.87 | 2/28/2001  | 0.31  | 1/31/2001  | 8.95  | 2/23/2001  | 8.12 | 6/11/1999 | 81  | 6/1/1999  | 172.5 |
| 2/13/2001  | 26.37 | 2/16/2001  | 42.41 | 3/5/2001   | 0.45  | 2/9/2001   | 10.37 | 2/28/2001  | 8.96 | 6/14/1999 | 82  | 6/2/1999  | 162.5 |
| 2/21/2001  | 24.99 | 2/23/2001  | 42.49 | 3/13/2001  | 0.02  | 2/16/2001  | 10.09 | 3/7/2001   | 7.87 | 6/15/1999 | 73  | 6/3/1999  | 245   |
| 2/28/2001  | 27.21 | 2/28/2001  | 42.15 | 3/19/2001  | 0.01  | 2/23/2001  | 9.83  | 3/16/2001  | 6.49 | 6/16/1999 | 76  | 6/4/1999  | 155   |
| 3/5/2001   | 24.1  | 3/7/2001   | 41.14 | 3/26/2001  | 0.17  | 2/28/2001  | 11.37 | 3/20/2001  | 7.20 | 6/17/1999 | 67  | 6/8/1999  | 195   |
| 3/13/2001  | 26.88 | 3/16/2001  | 40.31 | 4/2/2001   | 0.18  | 3/7/2001   | 9.75  | 3/29/2001  | 5.79 | 6/18/1999 | 76  | 6/9/1999  | 135   |
| 3/19/2001  | 24.45 | 3/20/2001  | 37.59 | 4/11/2001  | 0.76  | 3/16/2001  | 8.56  | 4/6/2001   | 7.41 | 6/20/1999 | 91  | 6/10/1999 | 122.5 |
| 3/26/2001  | 26.65 | 3/29/2001  | 28.53 | 4/17/2001  | 0.02  | 3/20/2001  | 8.97  | 4/13/2001  | 6.79 | 6/21/1999 | 91  | 6/11/1999 | 162.5 |
| 4/2/2001   | 24.23 | 4/6/2001   | 43.56 | 4/23/2001  | 0.00  | 3/29/2001  | 7.59  | 4/20/2001  | 5.73 | 6/22/1999 | 109 | 6/14/1999 | 132.5 |
| 4/11/2001  | 25.5  | 4/13/2001  | 37.95 | 5/1/2001   | 0.04  | 4/6/2001   | 9.49  | 4/27/2001  | 5.53 | 6/23/1999 | 64  | 6/15/1999 | 147.5 |
| 4/17/2001  | 29.79 | 4/20/2001  | 40.97 | 5/10/2001  | 0.01  | 4/13/2001  | 8.72  | 5/4/2001   | 5.76 | 6/24/1999 | 64  | 6/16/1999 | 127.5 |
| 4/23/2001  | 30.25 | 4/27/2001  | 38.76 | 5/16/2001  | 0.00  | 4/20/2001  | 7.30  | 5/9/2001   | 6.23 | 6/25/1999 | 82  | 6/17/1999 | 177.5 |
| 5/1/2001   | 26.81 | 5/4/2001   | 38.40 | 5/21/2001  | 0.00  | 4/27/2001  | 7.63  | 5/18/2001  | 4.92 | 6/26/1999 |     | 6/18/1999 | 152.5 |
| 5/10/2001  | 25.76 | 5/9/2001   | 42.95 | 5/28/2001  | 0.31  | 5/4/2001   | 7.00  | 5/25/2001  | 5.93 | 6/27/1999 |     | 6/21/1999 | 145   |
| 5/16/2001  | 31.39 | 5/18/2001  | 38.69 | 6/4/2001   | 0.02  | 5/9/2001   | 8.02  | 6/1/2001   | 6.53 | 6/28/1999 | 72  | 6/22/1999 | 105   |
| 5/21/2001  | 24.92 | 5/25/2001  | 38.03 | 6/12/2001  | 0.02  | 5/18/2001  | 6.23  | 6/8/2001   | 4.70 | 6/29/1999 | 71  | 6/23/1999 | 145   |
| 5/28/2001  | 24.36 | 5/31/2001  | 37.82 | 6/20/2001  | 0.02  | 5/25/2001  | 7.46  | 6/15/2001  | 5.45 | 6/30/1999 | 76  | 6/24/1999 | 140   |
| 6/4/2001   | 20.8  | 6/8/2001   | 35.47 | 6/27/2001  | 0.01  | 5/31/2001  | 8.23  | 6/22/2001  | 3.91 | 7/1/1999  | 79  | 6/25/1999 | 95    |
| 6/12/2001  | 24.54 | 6/15/2001  | 39.04 | 7/3/2001   | 0.02  | 6/8/2001   | 6.49  | 6/29/2001  | 4.29 | 7/2/1999  | 81  | 6/28/1999 | 100   |
| 6/20/2001  | 24.13 | 6/22/2001  | 32.75 | 7/10/2001  | 0.00  | 6/15/2001  | 6.96  | 7/6/2001   | 5.19 | 7/3/1999  |     | 6/29/1999 | 107.5 |
| 6/27/2001  | 26.27 | 6/29/2001  | 36.58 | 7/16/2001  | 0.01  | 6/22/2001  | 5.52  | 7/12/2001  | 4.51 | 7/4/1999  |     | 6/30/1999 | 105   |
| 7/3/2001   | 23.87 | 7/6/2001   | 37.35 | 7/23/2001  | 1.63  | 6/29/2001  | 5.96  | 7/19/2001  | 4.71 | 7/5/1999  | 102 | 7/1/1999  | 150   |
| 7/10/2001  | 23.93 | 7/9/2001   | 28.23 | 8/1/2001   | 0.04  | 7/6/2001   | 6.86  | 7/27/2001  | 5.17 | 7/6/1999  | 104 | 7/2/1999  | 135   |
| 7/16/2001  | 23.79 | 7/18/2001  | 35.29 | 8/7/2001   | 0.01  | 7/9/2001   | 5.47  | 8/1/2001   | 4.20 | 7/7/1999  | 99  | 7/5/1999  | 105   |
| 8/1/2001   | 24.87 | 7/27/2001  | 33.19 | 8/16/2001  | 0.00  | 7/18/2001  | 5.93  | 8/10/2001  | 4.62 | 7/8/1999  |     | 7/6/1999  | 105   |
| 8/7/2001   | 22.75 | 8/1/2001   | 33.89 | 8/20/2001  | 0.02  | 7/27/2001  | 6.17  | 8/15/2001  | 5.81 | 7/9/1999  | 84  | 7/7/1999  | 162.5 |
| 8/7/2001   | 22.09 | 8/10/2001  | 37.64 | 8/27/2001  | 0.04  | 8/1/2001   | 5.97  | 8/24/2001  | 5.12 | 7/10/1999 |     | 7/8/1999  | 135   |
| 8/16/2001  | 31.39 | 8/16/2001  | 35.02 | 9/4/2001   | 0.02  | 8/10/2001  | 5.76  | 9/1/2001   | 5.94 | 7/11/1999 |     | 7/9/1999  | 125   |
| 8/20/2001  | 22.67 | 8/24/2001  | 34.30 | 9/13/2001  | 0.08  | 8/16/2001  | 5.93  | 9/7/2001   | 4.66 | 7/12/1999 | 89  | 7/12/1999 | 92.5  |
| 8/27/2001  | 19.33 | 9/7/2001   | 34.54 | 9/17/2001  | 0.40  | 8/24/2001  | 6.51  | 9/12/2001  | 4.81 | 7/13/1999 | 107 | 7/13/1999 | 125   |
| 9/4/2001   | 24.73 | 9/14/2001  | 34.86 | 10/3/2001  | 0.03  | 8/28/2001  | 6.36  | 9/18/2001  | 5.71 | 7/14/1999 | 91  | 7/14/1999 | 135   |
| 9/13/2001  | 25.59 | 9/18/2001  | 37.83 | 10/10/2001 | 0.00  | 9/7/2001   | 6.04  | 9/28/2001  | 5.82 | 7/15/1999 |     | 7/15/1999 | 115   |
| 9/17/2001  | 21.87 | 9/28/2001  | 36.72 | 10/25/2001 | 0.01  | 9/14/2001  | 8.14  | 10/5/2001  | 5.98 | 7/16/1999 |     | 7/16/1999 | 172.5 |
| 10/3/2001  | 27.92 | 10/5/2001  | 39.36 | 10/31/2001 | 0.00  | 9/18/2001  | 8.12  | 10/12/2001 | 7.53 | 7/19/1999 | 95  | 7/19/1999 | 140   |
| 10/10/2001 | 28.72 | 10/12/2001 | 42.41 | 11/14/2001 | 0.00  | 9/28/2001  | 7.70  | 10/17/2001 | 7.77 | 7/20/1999 |     | 7/20/1999 |       |
| 10/25/2001 | 30.42 | 10/17/2001 | 43.39 | 11/21/2001 | 0.02  | 10/5/2001  | 7.70  | 10/25/2001 | 7.37 | 7/21/1999 | 86  | 7/21/1999 | 165   |
| 10/31/2001 | 29.47 | 10/25/2001 | 43.25 | 11/29/2001 | 0.35  | 10/12/2001 | 4.56  | 10/30/2001 | 6.54 | 7/22/1999 | 90  | 7/22/1999 | 160   |
| 11/14/2001 | 27.45 | 10/30/2001 | 39.90 | 12/3/2001  | 0.19  | 10/17/2001 | 9.77  | 11/9/2001  | 6.19 | 7/23/1999 | 81  | 7/23/1999 | 160   |
| 11/21/2001 | 29.03 | 11/6/2001  | 39.29 | 12/12/2001 | 0.37  | 10/25/2001 | 9.48  | 11/16/2001 | 6.78 | 7/26/1999 | 92  | 7/26/1999 | 127.5 |
| 11/29/2001 | 26.38 | 11/16/2001 | 38.90 | 12/17/2001 | 0.34  | 10/30/2001 | 8.65  | 11/23/2001 | 5.51 | 7/27/1999 |     | 7/27/1999 | 109.5 |
| 12/5/2001  | 25.46 | 11/23/2001 | 33.77 | 12/26/2001 | 0.04  | 11/6/2001  | 4.01  | 11/30/2001 | 7.54 | 7/28/1999 |     | 7/28/1999 | 132.5 |
| 12/12/2001 | 28.08 | 11/30/2001 | 42.43 | 1/2/2002   | 0.02  | 11/16/2001 | 8.78  | 12/7/2001  | 6.85 | 7/29/1999 | 80  | 7/29/1999 | 140   |
| 12/17/2001 | 26.02 | 12/7/2001  | 39.68 | 1/10/2002  | 0.12  | 11/23/2001 | 7.05  | 12/14/2001 | 7.44 | 7/30/1999 | 71  | 7/30/1999 | 122.5 |
| 12/26/2001 | 22.23 | 12/14/2001 | 40.85 | 1/16/2002  | 0.20  | 11/30/2001 | 9.54  | 12/20/2001 | 7.00 | 8/2/1999  | 101 | 8/1/1999  |       |
| 1/2/2002   | 26.79 | 12/20/2001 | 43.96 | 1/23/2002  | 0.43  | 12/7/2001  | 9.10  | 12/28/2001 | 5.81 | 8/3/1999  | 85  | 8/2/1999  | 132.5 |
| 1/10/2002  | 27.54 | 12/28/2001 | 41.65 | 2/6/2002   | 0.24  | 12/14/2001 | 10.85 | 1/4/2002   | 5.55 | 8/4/1999  | 86  | 8/3/1999  | 112.5 |
| 1/16/2002  | 27.83 | 1/4/2002   | 39.98 | 2/13/2002  | 0.08  | 12/20/2001 | 9.78  | 1/11/2002  | 5.42 | 8/5/1999  | 101 | 8/4/1999  | 95    |
| 1/23/2002  | 27.99 | 1/11/2002  | 39.17 | 2/20/2002  | 0.04  | 12/28/2001 | 7.87  | 1/18/2002  | 6.48 | 8/6/1999  |     | 8/5/1999  | 87.5  |
| 2/6/2002   | 23.14 | 1/18/2002  | 39.32 | 3/13/2002  | 0.23  | 1/4/2002   | 8.64  | 1/25/2002  | 5.82 | 8/9/1999  |     | 8/6/1999  |       |
| 2/13/2002  | 29.17 | 1/25/2002  | 38.69 | 3/18/2002  | 0.40  | 1/11/2002  | 8.56  | 2/1/2002   | 5.87 | 8/10/1999 |     | 8/7/1999  |       |
| 2/20/2002  | 28.43 | 2/4/2002   | 38.40 | 4/3/2002   | 0.04  | 1/18/2002  | 8.40  | 2/7/2002   | 5.45 | 8/11/1999 | 95  | 8/8/1999  |       |
| 3/13/2002  | 27.07 | 2/15/2002  | 42.18 | 4/8/2002   | 0.03  | 1/25/2002  | 7.99  | 2/15/2002  | 6.05 | 8/12/1999 | 61  | 8/9/1999  |       |
| 3/19/2002  | 21.41 | 2/22/2002  | 41.98 | 2/19/2002  | 8.15  | 2/4/2002   | 7.41  | 2/22/2002  | 5.52 | 8/13/1999 | 109 | 8/10/1999 |       |
| 4/3/2002   | 28.43 | 2/28/2002  | 41.96 | 2/22/2002  | 8.03  | 2/15/2002  | 8.15  | 2/28/2002  | 5.98 | 8/16/1999 | 54  | 8/11/1999 | 115   |
| 4/8/2002   | 26.93 | 3/7/2002   | 39.95 | 2/26/2002  | 8.40  | 2/22/2002  | 8.03  | 3/7/2002   | 6.96 | 8/17/1999 | 89  | 8/12/1999 | 142.5 |
| 4/7/2002   | 34.41 | 3/14/2002  | 43.30 | 3/7/2002   | 9.33  | 2/26/2002  | 8.40  | 3/14/2002  | 7.31 | 8/18/1999 | 101 | 8/13/1999 | 187.5 |
| 08/09/02   | 16.94 | 3/20/2002  | 43.91 | 3/14/2002  | 10.12 | 3/7/2002   | 9.33  | 3/20/2002  | 8.67 | 8/19/1999 | 70  | 8/14/1999 |       |
| 08/13/02   | 16.72 | 3/27/2002  | 44.64 | 6/3/2002   | 0.02  | 3/14/2002  | 10.12 | 3/27/2002  | 8.47 | 8/20/1999 | 75  | 8/15/1999 |       |
| 5/7/2002   | 27.7  | 4/2/2002   | 44.31 | 6/12/2002  | 0.04  | 3/20/2002  | 11.51 | 4/4/2002   | 8.77 | 8/23/1999 | 73  | 8/16/1999 | 95    |
| 5/22/2002  | 22.52 | 5/17/2002  | 43.99 | 6/19/2002  | 0.23  | 3/27/2002  | 11.06 | 4/9/2002   | 7.92 | 8/24/1999 | 70  | 8/17/1999 | 277.5 |
| 6/3/2002   | 21.93 | 5/29/2002  | 38.36 | 7/3/2002   | 1.07  | 4/2/2002   | 11.81 | 4/18/2002  | 6.64 | 8/25/1999 | 60  | 8/18/1999 | 182.5 |
| 6/10/2002  | 19.51 | 6/14/2002  | 32.85 | 7/10/2002  | 0.05  | 4/9/2002   | 11.65 | 4/26/2002  | 5.65 | 8/26/1999 | 67  | 8/19/1999 | 110   |
| 6/19/2002  | 21.52 | 6/20/2002  | 33.65 | 7/29/2002  | 0.02  | 4/18/2002  | 8.73  | 5/2/2002   | 4.97 | 8/27/1999 |     | 8/20/1999 | 170   |
| 7/3/2002   | 19.88 | 6/28/2002  | 27.48 | 8/5/2002   | 0.05  | 4/26/2002  | 8.29  | 5/8/2002   | 4.45 | 8/30/1999 |     | 8/23/1999 | 115   |
| 7/10/2002  | 21.22 | 7/12/2002  | 30.91 | 8/28/2002  | 0.13  | 5/2/2002   | 7.52  | 5/17/2002  | 6.13 | 8/31/1999 | 77  | 8/24/1999 | 87.5  |
| 7/29/2002  | 20.02 | 7/19/2002  | 32.15 | 9/9/2002   | 0.05  | 5/17/2002  | 7.42  | 5/20/2002  | 4.1  | 9/1/1999  | 96  | 8/25/1999 | 95    |
| 8/5/2002   | 18.56 | 7/23/2002  | 36.99 | 9/25/2002  | 0.02  | 5/20/2002  | 5.28  | 5/29/2002  | 5.14 | 9/2/1999  | 85  | 8/26/1999 | 107.5 |
| 8/28/2002  | 23.1  | 8/22/2002  | 17.36 | 10/2/2002  | 0.02  | 5/29/2002  | 5.26  | 6/7/2002   | 4.29 | 9/3/1999  | 84  | 8/27/1999 | 80    |
| 9/9/2002   | 23.07 | 8/26/2002  | 14.76 | 10/16/2002 | 0.00  | 6/14/2002  | 3.06  | 6/14/2002  | 4.12 | 9/6/1999  | 94  | 8/30/1999 | 152.5 |
| 9/25/2002  | 28.95 | 9/6/2002   | 36.20 | 10/30/2002 | 0.66  | 6/20/2002  | 6.33  | 6/20/2002  | 4.21 | 9/7/1999  | 92  | 8/31/1999 | 160   |
| 10/2/2002  | 29.96 | 9/12/2002  | 36.52 | 11/13/2002 | 0.81  | 6/28/2002  | 5.40  | 6/         |      |           |     |           |       |



|           |        |            |       |            |        |            |       |            |       |
|-----------|--------|------------|-------|------------|--------|------------|-------|------------|-------|
| 3/12/2003 | 43.13  | 12/24/2002 | 9.19  | 12/27/2002 | 5.77   | 10/13/1999 | 77    | 10/6/1999  | 160   |
| 3/21/2003 | 44.24  | 1/2/2003   | 8.67  | 1/3/2003   | 6.26   | 10/14/1999 | 118   | 10/7/1999  | 160   |
| 3/25/2003 | 42.74  | 1/10/2003  | 9.28  | 1/10/2003  | 6.66   | 10/15/1999 | 127   | 10/8/1999  | 190   |
| 4/4/2003  | 46.13  | 1/17/2003  | 8.07  | 1/17/2003  | 5.67   | 10/18/1999 | 0     | 10/11/1999 | 222.5 |
| 4/11/2003 | 39.82  | 1/23/2003  | 8.95  | 1/23/2003  | 6.84   | 10/19/1999 | 107   | 10/12/1999 | 212.5 |
| 4/18/2003 | 43.62  | 1/27/2003  | 8.87  | 1/30/2003  | 7.16   | 10/20/1999 | 87    | 10/13/1999 | 230   |
| 4/25/2003 | 45.98  | 2/4/2003   | 9.29  | 2/7/2003   | 7.05   | 10/21/1999 | 116   | 10/14/1999 | 257.5 |
| 4/28/2003 | 40.12  | 2/14/2003  | 9.75  | 2/14/2003  | 6.75   | 10/22/1999 | 82    | 10/15/1999 | 292.5 |
| 5/9/2003  | 45.64  | 2/21/2003  | 9.98  | 2/21/2003  | 7.15   | 10/25/1999 |       | 10/18/1999 | 250   |
| 5/15/2003 | 40.89  | 2/25/2003  | 10.76 | 2/28/2003  | 7.95   | 10/26/1999 | 111   | 10/19/1999 | 170   |
| 5/23/2003 | 40.93  | 3/7/2003   | 9.13  | 3/7/2003   | 6.64   | 10/27/1999 | 104   | 10/20/1999 | 195   |
| 5/27/2003 | 31.03  | 3/12/2003  | 9.39  | 3/12/2003  | 6.15   | 10/28/1999 | 99    | 10/21/1999 | 192.5 |
| Mean      | 36.73  | 3/21/2003  | 8.98  | 3/21/2003  | 6.38   | 10/29/1999 | 95    | 10/22/1999 | 185   |
| Median    | 37.22  | 3/25/2003  | 8.66  | 3/28/2003  | 6.00   | 11/1/1999  | 95    | 10/27/1999 | 192.5 |
| Max       | 48.56  | 4/4/2003   | 8.11  | 4/4/2003   | 5.57   | 11/2/1999  | 123   | 10/28/1999 | 185   |
| Min       | 14.76  | 4/11/2003  | 7.79  | 4/11/2003  | 4.85   | 11/3/1999  | 107   | 10/29/1999 | 215   |
| StnDev    | 5.72   | 4/18/2003  | 7.23  | 4/18/2003  | 4.22   | 11/4/1999  | 82    | 11/1/1999  | 170   |
| %Dev      | 15.37% | 4/25/2003  | 6.90  | 4/25/2003  | 4.54   | 11/5/1999  | 127   | 11/2/1999  | 202.5 |
|           |        | 4/28/2003  | 6.82  | 4/29/2003  | 2.26   | 11/8/1999  |       | 11/3/1999  | 225   |
|           |        | 5/9/2003   | 7.30  | Mean       | 5.87   | 11/9/1999  |       | 11/4/1999  | 175   |
|           |        | 5/15/2003  | 7.68  | Median     | 5.79   | 11/10/1999 |       | 11/5/1999  | 255   |
|           |        | 5/23/2003  | 7.56  | Max        | 9.86   | 11/11/1999 |       | 11/8/1999  | 267.5 |
|           |        | 5/27/2003  | 5.35  | Min        | 2.26   | 11/12/1999 | 143   | 11/9/1999  | 172.5 |
|           |        |            |       | StnDev     | 1.20   | 11/15/1999 | 148   | 11/10/1999 |       |
|           |        |            |       | %Dev       | 20.71% | 11/16/1999 | 121   | 11/11/1999 |       |
|           |        |            |       |            |        | 11/17/1999 |       | 11/12/1999 | 272.5 |
|           |        |            |       |            |        | 11/18/1999 |       | 11/15/1999 | 258.8 |
|           |        |            |       |            |        | 11/19/1999 | 78    | 11/16/1999 | 270   |
|           |        |            |       |            |        | 11/22/1999 | 86    | 11/17/1999 | 312.5 |
|           |        |            |       |            |        | 11/23/1999 | 96    | 11/18/1999 | 300   |
|           |        |            |       |            |        | 11/24/1999 | 104   | 11/19/1999 | 222.5 |
|           |        |            |       |            |        | 11/25/1999 | 89    | 11/22/1999 | 197.5 |
|           |        |            |       |            |        | 11/26/1999 | 82    | 11/23/1999 | 215   |
|           |        |            |       |            |        | 11/28/1999 | 106   | 11/24/1999 | 220   |
|           |        |            |       |            |        | 11/29/1999 | 83    | 11/25/1999 | 210   |
|           |        |            |       |            |        | 12/1/1999  |       | 11/26/1999 | 190   |
|           |        |            |       |            |        | 12/2/1999  | 97    | 11/29/1999 | 215   |
|           |        |            |       |            |        | 12/3/1999  | 73    | 11/30/1999 | 240   |
|           |        |            |       |            |        | 12/6/1999  | 85    | 12/1/1999  |       |
|           |        |            |       |            |        | 12/7/1999  | 91    | 12/2/1999  | 250   |
|           |        |            |       |            |        | 12/8/1999  | 107   | 12/3/1999  | 205   |
|           |        |            |       |            |        | 12/9/1999  | 88    | 12/6/1999  | 212.5 |
|           |        |            |       |            |        | 12/10/1999 | 92    | 12/7/1999  | 215   |
|           |        |            |       |            |        | 12/13/1999 | 107   | 12/8/1999  | 230   |
|           |        |            |       |            |        | 12/14/1999 | 103   | 12/9/1999  | 172.5 |
|           |        |            |       |            |        | 12/15/1999 | 84    | 12/10/1999 | 170   |
|           |        |            |       |            |        | 12/16/1999 | 78    | 12/13/1999 | 215   |
|           |        |            |       |            |        | 12/17/1999 | 74    | 12/14/1999 |       |
|           |        |            |       |            |        | 12/20/1999 | 115   | 12/15/1999 |       |
|           |        |            |       |            |        | 12/21/1999 | 114   | 12/16/1999 |       |
|           |        |            |       |            |        | 12/22/1999 | 129   | 12/17/1999 | 170   |
|           |        |            |       |            |        | 12/23/1999 | 120   | 12/20/1999 | 187.5 |
|           |        |            |       |            |        | 12/24/1999 | 97    | 12/21/1999 |       |
|           |        |            |       |            |        | 12/27/1999 | 145   | 12/22/1999 | 185   |
|           |        |            |       |            |        | 12/28/1999 | 128   | 12/23/1999 | 252.5 |
|           |        |            |       |            |        | 12/29/1999 | 115   | 12/24/1999 | 167.5 |
|           |        |            |       |            |        | 12/30/1999 | 107   | 12/27/1999 | 212.5 |
|           |        |            |       |            |        | 12/31/1999 | 138   | 12/28/1999 | 190   |
|           |        |            |       |            |        | 1/3/2000   |       | 12/29/1999 | 210   |
|           |        |            |       |            |        | 1/4/2000   | 128   | 12/30/1999 | 182.5 |
|           |        |            |       |            |        | 1/5/2000   | 85    | 12/31/1999 | 227.5 |
|           |        |            |       |            |        | 1/6/2000   | 95    | 1/3/2000   |       |
|           |        |            |       |            |        | 1/10/2000  | 93    | 1/4/2000   | 262.5 |
|           |        |            |       |            |        | 1/12/2000  | 98    | 1/5/2000   | 235   |
|           |        |            |       |            |        | 1/14/2000  | 85    | 1/6/2000   | 140   |
|           |        |            |       |            |        | 1/15/2000  |       | 1/7/2000   | 255   |
|           |        |            |       |            |        | 1/18/2000  | 90    | 1/10/2000  | 222.5 |
|           |        |            |       |            |        | 1/19/2000  | 83    | 1/11/2000  | 195   |
|           |        |            |       |            |        | 1/20/2000  | 110   | 1/12/2000  | 192.5 |
|           |        |            |       |            |        | 1/21/2000  | 93    | 1/13/2000  | 190   |
|           |        |            |       |            |        | 1/24/2000  | 103   | 1/14/2000  | 140   |
|           |        |            |       |            |        | 1/25/2000  | 106   | 1/18/2000  | 147.5 |
|           |        |            |       |            |        | 1/26/2000  | 85    | 1/19/2000  | 160   |
|           |        |            |       |            |        | 1/27/2000  | 75    | 1/20/2000  | 210   |
|           |        |            |       |            |        | 1/28/2000  | 92    | 1/21/2000  | 195   |
|           |        |            |       |            |        | 1/31/2000  | 106   | 1/24/2000  | 240   |
|           |        |            |       |            |        | 2/1/2000   | 156   | 1/25/2000  | 215   |
|           |        |            |       |            |        | 2/2/2000   | 176   | 1/26/2000  | 182.5 |
|           |        |            |       |            |        | 2/3/2000   | 113   | 1/27/2000  | 155   |
|           |        |            |       |            |        | 2/4/2000   | 157   | 1/28/2000  | 195   |
|           |        |            |       |            |        | 2/7/2000   | 130   | 1/31/2000  | 220   |
|           |        |            |       |            |        | 2/8/2000   | 124   | 2/1/2000   |       |
|           |        |            |       |            |        | 2/9/2000   | 98    | 2/2/2000   | 207.5 |
|           |        |            |       |            |        | 2/10/2000  | 102   | 2/3/2000   | 222.5 |
|           |        |            |       |            |        | 2/11/2000  | 104   | 2/4/2000   | 250   |
|           |        |            |       |            |        | 2/14/2000  | 105   | 2/7/2000   | 202.5 |
|           |        |            |       |            |        | 2/15/2000  | 107   | 2/8/2000   | 207.5 |
|           |        |            |       |            |        | 2/16/2000  | 103   | 2/9/2000   | 180   |
|           |        |            |       |            |        | 2/17/2000  | 92    | 2/10/2000  | 167.5 |
|           |        |            |       |            |        | 2/18/2000  | 105   | 2/11/2000  | 170   |
|           |        |            |       |            |        | 2/21/2000  | 129   | 2/14/2000  | 182.5 |
|           |        |            |       |            |        | 2/22/2000  | 98    | 2/15/2000  | 110   |
|           |        |            |       |            |        | 2/23/2000  | 162   | 2/16/2000  | 182.5 |
|           |        |            |       |            |        | 2/24/2000  | 150   | 2/17/2000  | 145   |
|           |        |            |       |            |        | 2/25/2000  | 116   | 2/18/2000  | 177.5 |
|           |        |            |       |            |        | 2/26/2000  | 183.5 | 2/21/2000  | 205   |
|           |        |            |       |            |        | 2/29/2000  | 117   | 2/22/2000  | 210   |
|           |        |            |       |            |        | 3/1/2000   | 109   | 2/23/2000  | 220   |
|           |        |            |       |            |        | 3/2/2000   | 156   | 2/24/2000  | 242.5 |
|           |        |            |       |            |        | 3/3/2000   | 111   | 2/25/2000  | 190   |

|  |  |  |  |  |  |           |       |           |       |
|--|--|--|--|--|--|-----------|-------|-----------|-------|
|  |  |  |  |  |  | 3/6/2000  | 124   | 2/28/2000 | 262.5 |
|  |  |  |  |  |  | 3/7/2000  | 143   | 2/29/2000 | 235   |
|  |  |  |  |  |  | 3/8/2000  | 130   | 3/1/2000  | 200   |
|  |  |  |  |  |  | 3/9/2000  | 114   | 3/2/2000  | 237.5 |
|  |  |  |  |  |  | 3/10/2000 | 133   | 3/3/2000  | 235   |
|  |  |  |  |  |  | 3/13/2000 | 108   | 3/6/2000  | 120   |
|  |  |  |  |  |  | 3/14/2000 | 121   | 3/7/2000  | 285   |
|  |  |  |  |  |  | 3/15/2000 | 122   | 3/8/2000  | 222.5 |
|  |  |  |  |  |  | 3/16/2000 | 87    | 3/9/2000  | 190   |
|  |  |  |  |  |  | 3/17/2000 | 115   | 3/10/2000 | 227.5 |
|  |  |  |  |  |  | 3/20/2000 | 115   | 3/13/2000 | 162.5 |
|  |  |  |  |  |  | 3/21/2000 | 103   | 3/14/2000 | 190   |
|  |  |  |  |  |  | 3/22/2000 | 138   | 3/15/2000 | 210   |
|  |  |  |  |  |  | 3/23/2000 | 121   | 3/16/2000 | 182.5 |
|  |  |  |  |  |  | 3/24/2000 | 106   | 3/17/2000 | 220   |
|  |  |  |  |  |  | 3/27/2000 | 105   | 3/20/2000 | 165   |
|  |  |  |  |  |  | 3/28/2000 | 119   | 3/21/2000 | 197.5 |
|  |  |  |  |  |  | 3/29/2000 | 100   | 3/22/2000 | 195   |
|  |  |  |  |  |  | 3/30/2000 | 112   | 3/23/2000 | 222.5 |
|  |  |  |  |  |  | 3/31/2000 | 118   | 3/24/2000 | 239   |
|  |  |  |  |  |  | 4/2/2000  |       | 3/27/2000 | 267.5 |
|  |  |  |  |  |  | 4/3/2000  | 93    | 3/28/2000 | 235   |
|  |  |  |  |  |  | 4/4/2000  | 127   | 3/29/2000 | 205   |
|  |  |  |  |  |  | 4/5/2000  | 131   | 3/30/2000 | 255   |
|  |  |  |  |  |  | 4/6/2000  | 111   | 3/31/2000 | 257.5 |
|  |  |  |  |  |  | 4/7/2000  | 124   | 4/3/2000  | 247.5 |
|  |  |  |  |  |  | 4/10/2000 | 140   | 4/4/2000  | 292.5 |
|  |  |  |  |  |  | 4/11/2000 | 99    | 4/5/2000  |       |
|  |  |  |  |  |  | 4/12/2000 | 117.5 | 4/6/2000  |       |
|  |  |  |  |  |  | 4/13/2000 | 140   | 4/7/2000  |       |
|  |  |  |  |  |  | 4/17/2000 | 129   | 4/10/2000 | 345   |
|  |  |  |  |  |  | 4/18/2000 | 112   | 4/11/2000 | 330   |
|  |  |  |  |  |  | 4/19/2000 | 108   | 4/12/2000 | 430   |
|  |  |  |  |  |  | 4/20/2000 | 130   | 4/13/2000 | 370   |
|  |  |  |  |  |  | 4/21/2000 | 105   | 4/14/2000 |       |
|  |  |  |  |  |  | 4/24/2000 | 90    | 4/17/2000 | 450   |
|  |  |  |  |  |  | 4/25/2000 | 111   | 4/18/2000 | 335   |
|  |  |  |  |  |  | 4/26/2000 | 90    | 4/19/2000 | 235   |
|  |  |  |  |  |  | 4/27/2000 | 116   | 4/20/2000 | 260   |
|  |  |  |  |  |  | 4/28/2000 | 110   | 4/21/2000 | 245   |
|  |  |  |  |  |  | 5/1/2000  | 105   | 4/24/2000 | 195   |
|  |  |  |  |  |  | 5/2/2000  | 108   | 4/25/2000 | 270   |
|  |  |  |  |  |  | 5/3/2000  | 104   | 4/26/2000 | 205   |
|  |  |  |  |  |  | 5/4/2000  | 102   | 4/27/2000 | 225   |
|  |  |  |  |  |  | 5/5/2000  | 99.5  | 4/28/2000 | 227.5 |
|  |  |  |  |  |  | 5/8/2000  | 81    | 5/1/2000  | 185   |
|  |  |  |  |  |  | 5/9/2000  | 94    | 5/2/2000  | 137.5 |
|  |  |  |  |  |  | 5/10/2000 | 110   | 5/3/2000  | 210   |
|  |  |  |  |  |  | 5/11/2000 | 102   | 5/4/2000  | 200   |
|  |  |  |  |  |  | 5/12/2000 | 95    | 5/5/2000  | 185   |
|  |  |  |  |  |  | 5/15/2000 | 104   | 5/8/2000  | 182.5 |
|  |  |  |  |  |  | 5/16/2000 | 99    | 5/9/2000  | 217.5 |
|  |  |  |  |  |  | 5/17/2000 | 78    | 5/10/2000 | 225   |
|  |  |  |  |  |  | 5/18/2000 | 108   | 5/11/2000 | 232.5 |
|  |  |  |  |  |  | 5/19/2000 | 94    | 5/12/2000 | 225   |
|  |  |  |  |  |  | 5/22/2000 | 91    | 5/15/2000 | 265   |
|  |  |  |  |  |  | 5/23/2000 | 95    | 5/16/2000 | 285   |
|  |  |  |  |  |  | 5/24/2000 | 93    | 5/17/2000 | 185   |
|  |  |  |  |  |  | 5/25/2000 | 94    | 5/19/2000 | 247.5 |
|  |  |  |  |  |  | 5/26/2000 | 91    | 5/22/2000 | 234   |
|  |  |  |  |  |  | 5/29/2000 | 71    | 5/23/2000 | 212.5 |
|  |  |  |  |  |  | 5/30/2000 | 74.5  | 5/24/2000 | 277.5 |
|  |  |  |  |  |  | 5/31/2000 | 83    | 5/25/2000 | 297.5 |
|  |  |  |  |  |  | 6/1/2000  | 118   | 5/26/2000 | 252.5 |
|  |  |  |  |  |  | 6/2/2000  | 97    | 5/29/2000 | 240   |
|  |  |  |  |  |  | 6/5/2000  | 71    | 5/30/2000 | 205   |
|  |  |  |  |  |  | 6/6/2000  | 74    | 5/31/2000 | 170   |
|  |  |  |  |  |  | 6/7/2000  | 84    | 6/1/2000  | 230   |
|  |  |  |  |  |  | 6/8/2000  |       | 6/2/2000  | 205   |
|  |  |  |  |  |  | 6/9/2000  |       | 6/5/2000  | 207.5 |
|  |  |  |  |  |  | 6/12/2000 | 74    | 6/6/2000  | 147   |
|  |  |  |  |  |  | 6/13/2000 | 77    | 6/7/2000  | 165   |
|  |  |  |  |  |  | 6/14/2000 | 100   | 6/8/2000  |       |
|  |  |  |  |  |  | 6/15/2000 | 103   | 6/9/2000  |       |
|  |  |  |  |  |  | 6/16/2000 | 83    | 6/12/2000 | 190   |
|  |  |  |  |  |  | 6/19/2000 | 79    | 6/13/2000 | 157.5 |
|  |  |  |  |  |  | 6/20/2000 | 97    | 6/14/2000 | 177.5 |
|  |  |  |  |  |  | 6/21/2000 | 89    | 6/15/2000 | 205   |
|  |  |  |  |  |  | 6/22/2000 | 93    | 6/16/2000 | 165   |
|  |  |  |  |  |  | 6/23/2000 | 107   | 6/19/2000 | 135   |
|  |  |  |  |  |  | 6/26/2000 | 88    | 6/20/2000 | 167.5 |
|  |  |  |  |  |  | 6/27/2000 | 99    | 6/21/2000 | 162.5 |
|  |  |  |  |  |  | 6/28/2000 | 88    | 6/22/2000 | 195   |
|  |  |  |  |  |  | 6/29/2000 | 106   | 6/23/2000 | 200   |
|  |  |  |  |  |  | 6/30/2000 | 109   | 6/26/2000 | 145   |
|  |  |  |  |  |  | 7/3/2000  | 69    | 6/27/2000 | 165   |
|  |  |  |  |  |  | 7/4/2000  | 75    | 6/28/2000 | 135   |
|  |  |  |  |  |  | 7/5/2000  | 68    | 6/29/2000 | 210   |
|  |  |  |  |  |  | 7/6/2000  | 90    | 6/30/2000 | 210   |
|  |  |  |  |  |  | 7/7/2000  | 88    | 7/3/2000  | 142.5 |
|  |  |  |  |  |  | 7/10/2000 | 83    | 7/4/2000  | 162.5 |
|  |  |  |  |  |  | 7/11/2000 | 87.5  | 7/5/2000  | 142.5 |
|  |  |  |  |  |  | 7/12/2000 | 67    | 7/6/2000  | 167.5 |
|  |  |  |  |  |  | 7/13/2000 | 110   | 7/7/2000  | 172.5 |
|  |  |  |  |  |  | 7/14/2000 | 109   | 7/10/2000 | 172.5 |
|  |  |  |  |  |  | 7/17/2000 | 89    | 7/11/2000 | 172.5 |
|  |  |  |  |  |  | 7/18/2000 | 95    | 7/12/2000 | 155   |
|  |  |  |  |  |  | 7/19/2000 | 80    | 7/13/2000 | 225   |
|  |  |  |  |  |  | 7/20/2000 | 94    | 7/14/2000 | 225   |
|  |  |  |  |  |  | 7/21/2000 | 104   | 7/17/2000 | 177.5 |

|  |  |  |  |  |  |            |      |            |       |
|--|--|--|--|--|--|------------|------|------------|-------|
|  |  |  |  |  |  | 7/24/2000  | 100  | 7/18/2000  | 185   |
|  |  |  |  |  |  | 7/25/2000  | 79   | 7/19/2000  | 167.5 |
|  |  |  |  |  |  | 7/26/2000  | 108  | 7/20/2000  | 195   |
|  |  |  |  |  |  | 7/27/2000  | 103  | 7/21/2000  | 167.5 |
|  |  |  |  |  |  | 7/28/2000  | 97   | 7/24/2000  | 160   |
|  |  |  |  |  |  | 7/31/2000  | 84   | 7/25/2000  | 150   |
|  |  |  |  |  |  | 8/1/2000   | 82   | 7/26/2000  | 155   |
|  |  |  |  |  |  | 8/2/2000   | 53   | 7/27/2000  | 167.5 |
|  |  |  |  |  |  | 8/3/2000   | 72   | 7/28/2000  | 172.5 |
|  |  |  |  |  |  | 8/4/2000   | 69   | 7/31/2000  | 142.5 |
|  |  |  |  |  |  | 8/7/2000   | 106  | 8/1/2000   | 140   |
|  |  |  |  |  |  | 8/8/2000   | 77   | 8/2/2000   | 230   |
|  |  |  |  |  |  | 8/9/2000   | 81   | 8/3/2000   | 142.5 |
|  |  |  |  |  |  | 8/10/2000  | 80   | 8/4/2000   | 147.5 |
|  |  |  |  |  |  | 8/11/2000  | 79   | 8/7/2000   | 157.5 |
|  |  |  |  |  |  | 8/14/2000  | 79   | 8/8/2000   | 152.5 |
|  |  |  |  |  |  | 8/15/2000  | 79   | 8/9/2000   | 137.5 |
|  |  |  |  |  |  | 8/16/2000  | 69   | 8/10/2000  | 162.5 |
|  |  |  |  |  |  | 8/17/2000  | 83   | 8/11/2000  | 190   |
|  |  |  |  |  |  | 8/18/2000  | 76   | 8/14/2000  | 147.5 |
|  |  |  |  |  |  | 8/21/2000  | 80   | 8/15/2000  | 165   |
|  |  |  |  |  |  | 8/22/2000  | 76   | 8/16/2000  | 192.5 |
|  |  |  |  |  |  | 8/23/2000  | 75   | 8/17/2000  | 162.5 |
|  |  |  |  |  |  | 8/24/2000  | 77   | 8/18/2000  | 170   |
|  |  |  |  |  |  | 8/25/2000  | 85   | 8/21/2000  | 142.5 |
|  |  |  |  |  |  | 8/28/2000  | 70.5 | 8/22/2000  | 142.5 |
|  |  |  |  |  |  | 8/29/2000  | 64   | 8/23/2000  | 165   |
|  |  |  |  |  |  | 8/30/2000  | 63   | 8/24/2000  | 185   |
|  |  |  |  |  |  | 8/31/2000  | 76   | 8/25/2000  | 185   |
|  |  |  |  |  |  | 9/1/2000   | 83   | 8/28/2000  | 170   |
|  |  |  |  |  |  | 9/4/2000   | 65   | 8/29/2000  | 182.5 |
|  |  |  |  |  |  | 9/5/2000   | 85   | 8/30/2000  | 162.5 |
|  |  |  |  |  |  | 9/6/2000   | 86   | 8/31/2000  | 190   |
|  |  |  |  |  |  | 9/7/2000   | 70   | 9/1/2000   | 195   |
|  |  |  |  |  |  | 9/8/2000   | 105  | 9/4/2000   | 192.5 |
|  |  |  |  |  |  | 9/11/2000  | 95   | 9/5/2000   | 187.5 |
|  |  |  |  |  |  | 9/12/2000  | 96   | 9/6/2000   | 182.5 |
|  |  |  |  |  |  | 9/13/2000  | 77   | 9/7/2000   | 215   |
|  |  |  |  |  |  | 9/14/2000  | 94   | 9/8/2000   | 215   |
|  |  |  |  |  |  | 9/15/2000  | 84   | 9/11/2000  | 165   |
|  |  |  |  |  |  | 9/18/2000  | 101  | 9/12/2000  | 160   |
|  |  |  |  |  |  | 9/19/2000  | 91   | 9/13/2000  | 157.5 |
|  |  |  |  |  |  | 9/20/2000  | 82   | 9/14/2000  | 177.5 |
|  |  |  |  |  |  | 9/21/2000  | 90   | 9/15/2000  | 175   |
|  |  |  |  |  |  | 9/22/2000  | 79   | 9/16/2000  | 162.5 |
|  |  |  |  |  |  | 9/23/2000  |      | 9/19/2000  | 150   |
|  |  |  |  |  |  | 9/25/2000  | 75   | 9/20/2000  | 175   |
|  |  |  |  |  |  | 9/26/2000  | 84   | 9/21/2000  | 165   |
|  |  |  |  |  |  | 9/27/2000  | 85   | 9/22/2000  | 155   |
|  |  |  |  |  |  | 9/28/2000  | 84   | 9/25/2000  | 152.5 |
|  |  |  |  |  |  | 9/29/2000  | 107  | 9/26/2000  | 132.5 |
|  |  |  |  |  |  | 9/30/2000  |      | 9/27/2000  | 150   |
|  |  |  |  |  |  | 10/2/2000  | 109  | 9/28/2000  | 147.5 |
|  |  |  |  |  |  | 10/3/2000  | 85   | 9/29/2000  | 165   |
|  |  |  |  |  |  | 10/4/2000  | 90   | 10/2/2000  | 137.5 |
|  |  |  |  |  |  | 10/5/2000  | 81   | 10/3/2000  | 145   |
|  |  |  |  |  |  | 10/6/2000  | 93   | 10/4/2000  | 137.5 |
|  |  |  |  |  |  | 10/9/2000  | 99   | 10/5/2000  | 125   |
|  |  |  |  |  |  | 10/10/2000 | 86   | 10/6/2000  | 165   |
|  |  |  |  |  |  | 10/11/2000 | 91   | 10/9/2000  | 214   |
|  |  |  |  |  |  | 10/12/2000 | 86   | 10/10/2000 | 160   |
|  |  |  |  |  |  | 10/13/2000 | 128  | 10/11/2000 | 172.5 |
|  |  |  |  |  |  | 10/16/2000 | 93   | 10/12/2000 | 195   |
|  |  |  |  |  |  | 10/17/2000 | 89   | 10/13/2000 | 207.5 |
|  |  |  |  |  |  | 10/18/2000 | 87   | 10/16/2000 | 117.5 |
|  |  |  |  |  |  | 10/19/2000 | 100  | 10/17/2000 | 162.5 |
|  |  |  |  |  |  | 10/20/2000 | 101  | 10/18/2000 | 151.3 |
|  |  |  |  |  |  | 10/23/2000 | 95   | 10/19/2000 | 180   |
|  |  |  |  |  |  | 10/24/2000 | 88   | 10/20/2000 | 190   |
|  |  |  |  |  |  | 10/25/2000 | 81   | 10/23/2000 | 157.5 |
|  |  |  |  |  |  | 10/26/2000 | 93   | 10/24/2000 | 157.5 |
|  |  |  |  |  |  | 10/27/2000 | 100  | 10/25/2000 | 157.5 |
|  |  |  |  |  |  | 10/30/2000 | 94   | 10/26/2000 | 175   |
|  |  |  |  |  |  | 10/31/2000 | 88   | 10/27/2000 | 185   |
|  |  |  |  |  |  | 11/1/2000  | 100  | 10/30/2000 | 147.5 |
|  |  |  |  |  |  | 11/2/2000  | 78   | 10/31/2000 | 150   |
|  |  |  |  |  |  | 11/3/2000  | 93   | 11/1/2000  | 152.5 |
|  |  |  |  |  |  | 11/6/2000  | 99   | 11/2/2000  | 187.5 |
|  |  |  |  |  |  | 11/7/2000  | 98   | 11/3/2000  | 167.5 |
|  |  |  |  |  |  | 11/8/2000  | 84   | 11/6/2000  | 175   |
|  |  |  |  |  |  | 11/9/2000  | 108  | 11/7/2000  | 195   |
|  |  |  |  |  |  | 11/10/2000 | 97   | 11/8/2000  | 165   |
|  |  |  |  |  |  | 11/12/2000 |      | 11/9/2000  | 227.5 |
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|  |  |  |  |  |  | 10/1/2002  | 88  | 9/26/2002  | 182.5 |
|  |  |  |  |  |  | 10/2/2002  | 88  | 9/27/2002  | 180   |
|  |  |  |  |  |  | 10/3/2002  | 124 | 9/30/2002  | 142.5 |
|  |  |  |  |  |  | 10/4/2002  | 86  | 10/1/2002  | 122.5 |
|  |  |  |  |  |  | 10/7/2002  | 125 | 10/2/2002  | 150   |
|  |  |  |  |  |  | 10/8/2002  | 105 | 10/3/2002  | 162.5 |
|  |  |  |  |  |  | 10/9/2002  | 107 | 10/4/2002  | 160   |
|  |  |  |  |  |  | 10/10/2002 | 130 | 10/7/2002  | 160   |
|  |  |  |  |  |  | 10/11/2002 | 126 | 10/8/2002  | 182.5 |
|  |  |  |  |  |  | 10/14/2002 | 105 | 10/9/2002  | 157.5 |
|  |  |  |  |  |  | 10/15/2002 | 172 | 10/10/2002 | 190   |
|  |  |  |  |  |  | 10/16/2002 | 120 | 10/11/2002 | 190   |
|  |  |  |  |  |  | 10/17/2002 | 116 | 10/14/2002 | 167.5 |
|  |  |  |  |  |  | 10/18/2002 | 118 | 10/15/2002 | 152.5 |
|  |  |  |  |  |  | 10/21/2002 | 106 | 10/16/2002 | 145   |
|  |  |  |  |  |  | 10/22/2002 | 130 | 10/17/2002 | 160   |
|  |  |  |  |  |  | 10/23/2002 | 119 | 10/18/2002 | 177.5 |
|  |  |  |  |  |  | 10/24/2002 | 127 | 10/21/2002 | 200   |
|  |  |  |  |  |  | 10/25/2002 | 139 | 10/22/2002 | 192.5 |
|  |  |  |  |  |  | 10/28/2002 | 100 | 10/23/2002 | 182.5 |



|  |  |  |  |  |  |            |       |            |       |
|--|--|--|--|--|--|------------|-------|------------|-------|
|  |  |  |  |  |  | 10/29/2002 | 110   | 10/24/2002 | 182.5 |
|  |  |  |  |  |  | 10/30/2002 | 107   | 10/25/2002 | 182.5 |
|  |  |  |  |  |  | 10/31/2002 | 107   | 10/26/2002 | 150   |
|  |  |  |  |  |  | 11/1/2002  | 98    | 10/29/2002 | 135   |
|  |  |  |  |  |  | 11/4/2002  | 112   | 10/30/2002 | 140   |
|  |  |  |  |  |  | 11/5/2002  | 103   | 10/31/2002 | 170   |
|  |  |  |  |  |  | 11/6/2002  | 103   | 11/1/2002  | 137.5 |
|  |  |  |  |  |  | 11/7/2002  | 140   | 11/4/2002  | 160   |
|  |  |  |  |  |  | 11/8/2002  | 136   | 11/5/2002  | 160   |
|  |  |  |  |  |  | 11/11/2002 | 126   | 11/7/2002  | 180   |
|  |  |  |  |  |  | 11/12/2002 | 122   | 11/8/2002  | 183.8 |
|  |  |  |  |  |  | 11/13/2002 | 118   | 11/11/2002 | 155   |
|  |  |  |  |  |  | 11/14/2002 | 107   | 11/12/2002 | 165   |
|  |  |  |  |  |  | 11/15/2002 | 144   | 11/13/2002 | 160   |
|  |  |  |  |  |  | 11/18/2002 | 156   | 11/14/2002 | 156.3 |
|  |  |  |  |  |  | 11/19/2002 | 128   | 11/15/2002 | 170   |
|  |  |  |  |  |  | 11/20/2002 | 118   | 11/18/2002 | 155   |
|  |  |  |  |  |  | 11/21/2002 | 130   | 11/19/2002 | 167.5 |
|  |  |  |  |  |  | 11/22/2002 | 108   | 11/20/2002 | 132.5 |
|  |  |  |  |  |  | 11/25/2002 | 116.2 | 11/21/2002 | 166.3 |
|  |  |  |  |  |  | 11/26/2002 | 116.6 | 11/22/2002 | 192.5 |
|  |  |  |  |  |  | 11/27/2002 | 126.6 | 11/25/2002 | 192.5 |
|  |  |  |  |  |  | 11/28/2002 | 112   | 11/26/2002 | 192.5 |
|  |  |  |  |  |  | 11/29/2002 | 107   | 11/27/2002 | 172.5 |
|  |  |  |  |  |  | 12/2/2002  | 136.6 | 11/28/2002 | 175   |
|  |  |  |  |  |  | 12/3/2002  | 118.6 | 11/29/2002 | 155   |
|  |  |  |  |  |  | 12/4/2002  | 135.9 | 11/30/2002 |       |
|  |  |  |  |  |  | 12/5/2002  | 206.6 | 12/2/2002  | 177.5 |
|  |  |  |  |  |  | 12/6/2002  | 177.5 | 12/3/2002  | 240   |
|  |  |  |  |  |  | 12/9/2002  | 157.6 | 12/4/2002  | 167.5 |
|  |  |  |  |  |  | 12/10/2002 | 164.5 | 12/5/2002  | 200   |
|  |  |  |  |  |  | 12/11/2002 | 224   | 12/6/2002  | 260   |
|  |  |  |  |  |  | 12/12/2002 | 148   | 12/9/2002  | 340   |
|  |  |  |  |  |  | 12/13/2002 | 166   | 12/10/2002 | 245   |
|  |  |  |  |  |  | 12/16/2002 | 128   | 12/11/2002 | 215   |
|  |  |  |  |  |  | 12/17/2002 | 125   | 12/12/2002 | 172.5 |
|  |  |  |  |  |  | 12/18/2002 | 126   | 12/13/2002 | 182.5 |
|  |  |  |  |  |  | 12/19/2002 | 124   | 12/16/2002 | 293.8 |
|  |  |  |  |  |  | 12/20/2002 | 117.3 | 12/17/2002 | 320   |
|  |  |  |  |  |  | 12/23/2002 | 111   | 12/18/2002 | 182.5 |
|  |  |  |  |  |  | 12/24/2002 | 105.1 | 12/19/2002 | 202.5 |
|  |  |  |  |  |  | 12/25/2002 | 102.7 | 12/20/2002 |       |
|  |  |  |  |  |  | 12/26/2002 | 100   | 12/23/2002 | 217.5 |
|  |  |  |  |  |  | 12/27/2002 | 113   | 12/24/2002 | 192.5 |
|  |  |  |  |  |  | 12/30/2002 | 112.5 | 12/25/2002 | 367.5 |
|  |  |  |  |  |  | 12/31/2002 | 111   | 12/26/2002 | 150   |
|  |  |  |  |  |  | 1/1/2003   | 101   | 12/27/2002 | 362.5 |
|  |  |  |  |  |  | 1/2/2003   | 111   | 12/28/2002 |       |
|  |  |  |  |  |  | 1/3/2003   | 112.6 | 12/29/2002 |       |
|  |  |  |  |  |  | 1/6/2003   | 111   | 12/30/2002 | 345   |
|  |  |  |  |  |  | 1/7/2003   | 108   | 12/31/2002 |       |
|  |  |  |  |  |  | 1/8/2003   | 110   | 1/1/2003   | 167.5 |
|  |  |  |  |  |  | 1/9/2003   | 113   | 1/2/2003   | 175   |
|  |  |  |  |  |  | 1/10/2003  | 98    | 1/3/2003   | 217.5 |
|  |  |  |  |  |  | 1/13/2003  | 139.4 | 1/4/2003   |       |
|  |  |  |  |  |  | 1/14/2003  | 113.3 | 1/5/2003   |       |
|  |  |  |  |  |  | 1/15/2003  | 117.3 | 1/6/2003   | 205   |
|  |  |  |  |  |  | 1/16/2003  | 120   | 1/7/2003   | 178.8 |
|  |  |  |  |  |  | 1/17/2003  | 116   | 1/8/2003   | 102.5 |
|  |  |  |  |  |  | 1/20/2003  | 109   | 1/9/2003   | 152.5 |
|  |  |  |  |  |  | 1/21/2003  | 108   | 1/10/2003  | 187.5 |
|  |  |  |  |  |  | 1/22/2003  | 103   | 1/11/2003  |       |
|  |  |  |  |  |  | 1/23/2003  | 119   | 1/12/2003  |       |
|  |  |  |  |  |  | 1/24/2003  | 91    | 1/13/2003  | 180   |
|  |  |  |  |  |  | 1/27/2003  | 169.3 | 1/14/2003  | 142.5 |
|  |  |  |  |  |  | 1/28/2003  | 125.3 | 1/15/2003  | 125   |
|  |  |  |  |  |  | 1/29/2003  | 154.7 | 1/16/2003  | 142.5 |
|  |  |  |  |  |  | 1/30/2003  | 120   | 1/17/2003  | 135   |
|  |  |  |  |  |  | 1/31/2003  | 154.7 | 1/18/2003  |       |
|  |  |  |  |  |  | 2/3/2003   | 130.7 | 1/19/2003  |       |
|  |  |  |  |  |  | 2/4/2003   | 117.3 | 1/20/2003  | 165   |
|  |  |  |  |  |  | 2/5/2003   | 117.8 | 1/21/2003  | 185   |
|  |  |  |  |  |  | 2/6/2003   | 132   | 1/22/2003  | 137.5 |
|  |  |  |  |  |  | 2/7/2003   | 142.6 | 1/23/2003  | 165   |
|  |  |  |  |  |  | 2/10/2003  | 124   | 1/24/2003  | 165   |
|  |  |  |  |  |  | 2/11/2003  | 142.6 | 1/25/2003  |       |
|  |  |  |  |  |  | 2/12/2003  | 121.3 | 1/26/2003  |       |
|  |  |  |  |  |  | 2/13/2003  | 130.7 | 1/27/2003  | 167.5 |
|  |  |  |  |  |  | 2/14/2003  | 156   | 1/28/2003  |       |
|  |  |  |  |  |  | 2/17/2003  | 181.3 | 1/29/2003  | 195   |
|  |  |  |  |  |  | 2/18/2003  | 109.3 | 1/30/2003  | 166.3 |
|  |  |  |  |  |  | 2/19/2003  | 113   | 1/31/2003  | 217.5 |
|  |  |  |  |  |  | 2/20/2003  | 146.3 | 2/1/2003   |       |
|  |  |  |  |  |  | 2/21/2003  | 152.5 | 2/2/2003   |       |
|  |  |  |  |  |  | 2/24/2003  | 173.8 | 2/3/2003   | 190   |
|  |  |  |  |  |  | 2/25/2003  | 133.8 | 2/4/2003   | 147.5 |
|  |  |  |  |  |  | 2/26/2003  | 134.4 | 2/5/2003   | 170   |
|  |  |  |  |  |  | 2/27/2003  |       | 2/6/2003   | 143.8 |
|  |  |  |  |  |  | 2/28/2003  | 126.3 | 2/7/2003   | 167.5 |
|  |  |  |  |  |  | 3/3/2003   | 110   | 2/8/2003   |       |
|  |  |  |  |  |  | 3/4/2003   | 128.8 | 2/9/2003   |       |
|  |  |  |  |  |  | 3/5/2003   | 117.5 | 2/10/2003  | 162.5 |
|  |  |  |  |  |  | 3/6/2003   | 108.7 | 2/11/2003  | 175   |
|  |  |  |  |  |  | 3/7/2003   | 115   | 2/12/2003  | 115   |
|  |  |  |  |  |  | 3/10/2003  | 113.8 | 2/13/2003  | 150   |
|  |  |  |  |  |  | 3/11/2003  | 112.5 | 2/14/2003  | 167.5 |
|  |  |  |  |  |  | 3/12/2003  | 122.5 | 2/15/2003  |       |
|  |  |  |  |  |  | 3/13/2003  | 120   | 2/16/2003  |       |
|  |  |  |  |  |  | 3/14/2003  | 115   | 2/17/2003  | 160   |
|  |  |  |  |  |  | 3/17/2003  | 127.5 | 2/18/2003  | 142.5 |

|  |  |  |  |  |  |           |        |           |       |
|--|--|--|--|--|--|-----------|--------|-----------|-------|
|  |  |  |  |  |  | 3/18/2003 | 133.8  | 2/19/2003 | 155   |
|  |  |  |  |  |  | 3/19/2003 | 163.7  | 2/20/2003 | 155   |
|  |  |  |  |  |  | 3/20/2003 | 131.3  | 2/21/2003 | 180   |
|  |  |  |  |  |  | 3/21/2003 | 143.8  | 2/22/2003 |       |
|  |  |  |  |  |  | 3/24/2003 | 181.3  | 2/23/2003 |       |
|  |  |  |  |  |  | 3/25/2003 | 123.8  | 2/24/2003 | 182.5 |
|  |  |  |  |  |  | 3/26/2003 | 118.2  | 2/25/2003 | 162.5 |
|  |  |  |  |  |  | 3/27/2003 |        | 2/26/2003 | 177.5 |
|  |  |  |  |  |  | 3/28/2003 | 145    | 2/27/2003 |       |
|  |  |  |  |  |  | 3/31/2003 | 118.85 | 2/28/2003 | 157.5 |
|  |  |  |  |  |  | 4/1/2003  | 112.5  | 3/1/2003  |       |
|  |  |  |  |  |  | 4/2/2003  | 130    | 3/2/2003  |       |
|  |  |  |  |  |  | 4/3/2003  | 127.5  | 3/3/2003  | 185   |
|  |  |  |  |  |  | 4/4/2003  | 106.3  | 3/4/2003  | 167.5 |
|  |  |  |  |  |  | 4/7/2003  | 102.5  | 3/5/2003  | 185   |
|  |  |  |  |  |  | 4/8/2003  | 118.8  | 3/6/2003  | 170   |
|  |  |  |  |  |  | 4/9/2003  | 132.5  | 3/7/2003  | 172.5 |
|  |  |  |  |  |  | 4/10/2003 | 117.5  | 3/8/2003  |       |
|  |  |  |  |  |  | 4/11/2003 | 127.5  | 3/9/2003  |       |
|  |  |  |  |  |  | 4/13/2003 |        | 3/10/2003 | 222.5 |
|  |  |  |  |  |  | 4/14/2003 | 141.3  | 3/11/2003 | 227.5 |
|  |  |  |  |  |  | 4/15/2003 | 103.8  | 3/12/2003 | 170   |
|  |  |  |  |  |  | 4/16/2003 | 151.3  | 3/13/2003 | 175   |
|  |  |  |  |  |  | 4/17/2003 | 126.3  | 3/14/2003 | 150   |
|  |  |  |  |  |  | 4/18/2003 | 155.7  | 3/17/2003 | 152.5 |
|  |  |  |  |  |  | 4/21/2003 | 125.7  | 3/18/2003 | 162.5 |
|  |  |  |  |  |  | 4/22/2003 | 127.5  | 3/19/2003 | 165   |
|  |  |  |  |  |  | 4/23/2003 | 133.8  | 3/20/2003 | 177.5 |
|  |  |  |  |  |  | 4/24/2003 | 134.4  | 3/21/2003 |       |
|  |  |  |  |  |  | 4/25/2003 | 127.5  | 3/22/2003 |       |
|  |  |  |  |  |  | 4/28/2003 | 113.8  | 3/23/2003 |       |
|  |  |  |  |  |  | 4/29/2003 | 123.8  | 3/24/2003 | 185   |
|  |  |  |  |  |  | 4/30/2003 | 102.5  | 3/25/2003 | 170   |
|  |  |  |  |  |  | 5/1/2003  | 137.5  | 3/26/2003 | 157.5 |
|  |  |  |  |  |  | 5/2/2003  | 101.2  | 3/27/2003 |       |
|  |  |  |  |  |  | 5/5/2003  | 115    | 3/28/2003 | 155   |
|  |  |  |  |  |  | 5/6/2003  | 137.5  | 3/29/2003 |       |
|  |  |  |  |  |  | 5/7/2003  | 123.8  | 3/30/2003 |       |
|  |  |  |  |  |  | 5/8/2003  | 127.5  | 3/31/2003 | 175   |
|  |  |  |  |  |  | 5/9/2003  | 137.5  | 4/1/2003  | 182.5 |
|  |  |  |  |  |  | 5/12/2003 | 98.7   | 4/2/2003  | 187.5 |
|  |  |  |  |  |  | 5/13/2003 | 106.3  | 4/3/2003  | 185   |
|  |  |  |  |  |  | 5/14/2003 | 113.8  | 4/4/2003  | 140   |
|  |  |  |  |  |  | 5/15/2003 | 118.8  | 4/5/2003  |       |
|  |  |  |  |  |  | 5/16/2003 | 108.7  | 4/6/2003  |       |
|  |  |  |  |  |  | 5/19/2003 | 90     | 4/7/2003  | 152.5 |
|  |  |  |  |  |  | 5/20/2003 | 144    | 4/8/2003  | 167.5 |
|  |  |  |  |  |  | 5/21/2003 | 115.1  | 4/9/2003  | 175   |
|  |  |  |  |  |  | 5/22/2003 | 107.5  | 4/10/2003 | 210   |
|  |  |  |  |  |  | 5/23/2003 | 117.5  | 4/11/2003 | 170   |
|  |  |  |  |  |  | 5/26/2003 | 121.3  | 4/13/2003 |       |
|  |  |  |  |  |  | 5/27/2003 | 90     | 4/14/2003 | 167.5 |
|  |  |  |  |  |  | 5/28/2003 | 121.3  | 4/15/2003 | 180   |
|  |  |  |  |  |  | 5/29/2003 | 136.3  | 4/16/2003 | 160   |
|  |  |  |  |  |  | 5/30/2003 | 128.8  | 4/17/2003 | 147.5 |
|  |  |  |  |  |  | Mean      | 101.99 | 4/18/2003 | 150   |
|  |  |  |  |  |  | Median    | 99.00  | 4/19/2003 |       |
|  |  |  |  |  |  | Max       | 226.00 | 4/20/2003 |       |
|  |  |  |  |  |  | Min       | 0.00   | 4/21/2003 | 172.5 |
|  |  |  |  |  |  | StnDev    | 22.62  | 4/22/2003 | 200   |
|  |  |  |  |  |  | %Dev      | 22.85% | 4/23/2003 | 185   |
|  |  |  |  |  |  |           |        | 4/24/2003 | 187.5 |
|  |  |  |  |  |  |           |        | 4/25/2003 | 155   |
|  |  |  |  |  |  |           |        | 4/26/2003 |       |
|  |  |  |  |  |  |           |        | 4/27/2003 |       |
|  |  |  |  |  |  |           |        | 4/28/2003 | 192.5 |
|  |  |  |  |  |  |           |        | 4/29/2003 | 262.5 |
|  |  |  |  |  |  |           |        | 4/30/2003 | 217.5 |
|  |  |  |  |  |  |           |        | 5/1/2003  | 260   |
|  |  |  |  |  |  |           |        | 5/2/2003  | 155   |
|  |  |  |  |  |  |           |        | 5/3/2003  |       |
|  |  |  |  |  |  |           |        | 5/4/2003  |       |
|  |  |  |  |  |  |           |        | 5/5/2003  | 170   |
|  |  |  |  |  |  |           |        | 5/6/2003  | 177.5 |
|  |  |  |  |  |  |           |        | 5/7/2003  | 175   |
|  |  |  |  |  |  |           |        | 5/8/2003  | 175   |
|  |  |  |  |  |  |           |        | 5/9/2003  | 142.5 |
|  |  |  |  |  |  |           |        | 5/10/2003 |       |
|  |  |  |  |  |  |           |        | 5/11/2003 |       |
|  |  |  |  |  |  |           |        | 5/12/2003 | 160   |
|  |  |  |  |  |  |           |        | 5/13/2003 | 170   |
|  |  |  |  |  |  |           |        | 5/14/2003 | 167.5 |
|  |  |  |  |  |  |           |        | 5/15/2003 | 167.5 |
|  |  |  |  |  |  |           |        | 5/16/2003 | 177.5 |
|  |  |  |  |  |  |           |        | 5/17/2003 |       |
|  |  |  |  |  |  |           |        | 5/18/2003 |       |
|  |  |  |  |  |  |           |        | 5/19/2003 | 162.5 |
|  |  |  |  |  |  |           |        | 5/20/2003 | 145   |
|  |  |  |  |  |  |           |        | 5/21/2003 | 172.5 |
|  |  |  |  |  |  |           |        | 5/22/2003 | 167.5 |
|  |  |  |  |  |  |           |        | 5/23/2003 | 235   |
|  |  |  |  |  |  |           |        | 5/27/2003 | 115   |
|  |  |  |  |  |  |           |        | 5/28/2003 | 137.5 |
|  |  |  |  |  |  |           |        | 5/29/2003 | 142.5 |
|  |  |  |  |  |  |           |        | 5/30/2003 | 145   |
|  |  |  |  |  |  |           |        | 5/31/2003 | 0     |
|  |  |  |  |  |  | Mean      | 173.74 |           |       |
|  |  |  |  |  |  | Median    | 167.50 |           |       |
|  |  |  |  |  |  | Max       | 450.00 |           |       |
|  |  |  |  |  |  | Min       | 0.00   |           |       |
|  |  |  |  |  |  | StnDev    | 40.64  |           |       |
|  |  |  |  |  |  | %Dev      | 24.26% |           |       |

## Missoula WWTP Influent Metal Concentrations

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## Missoula WWTP Sludge Metals Concentration

| Missoula WWTP Sludge Metals Concentration |           |          |        |       |      |        |       |            |       |            |        |           |         |         |         |
|---|-----------|----------|--------|-------|------|--------|-------|------------|-------|------------|--------|-----------|---------|---------|---------|
| Sludge                                    | As        |          | Cd     |       | Cr   |        | Cu    |            | Pb    | Hg         | Mo     | Ni        | Se      | Au      | Zn      |
|   | ≤         |          | ≤      |       | ≤    |        | ≤     |            | ≤     | ≤          | ≤      | ≤         | ≤       | ≤       | ≤       |
| 08/30/93                                  | 0.25      | 5.4      |        |       | 38.5 |        | 710   |            | 149   | 0.25       | 19     | 25.1      | 0.45    | X       | 8850    |
| 11/17/93                                  | 0.15      | 9.1      |        |       | 45.5 |        | 996   |            | 270   | 0.21       | 60.5   | 41.5      | 0.44    | X       | 1120    |
| 02/07/95                                  | 1.7       | 4.43     | 5.6    |       | 562  |        | 562   |            | 16    | 0.23       | 16     | 22.6      | 7.23    | 0.25 <5 | 618     |
| 08/24/95                                  | 1.5       | 4.9      | 155    |       | 798  |        | 40.2  |            | 0.18  | 1.25 <.001 | 22.7   | 3         | 0.25 <5 | 1117    |         |
| 10/30/95                                  | 1.5       | 0.73     |        | 28    |      | 118.4  | 7.4   | 0.005 <.01 |       | 14.5       | 2.7    | 4.7       | 1.1     | 2.5     | 60      |
| 12/26/95                                  | 1.4       | 4.85     |        | 47.8  |      | 695    |       | 0.005 <.01 |       | 23.2       | 2.2    | 4.6       | 4.6     | 37.3    | 798     |
| 03/18/96                                  | 2.5 <5    |          | 34.5   |       | X    |        | 100   |            | 2     | 11         | 20.5   | 2.5 <5    | 125     |         | 825     |
| 07/16/96                                  | 2.8       | 0.5      | 4.9    |       | 110  |        | 23    |            | 4.8   | 1 <2       |        | 2         | 1 <2    | 15      | 85      |
| 10/24/96                                  | 2.5 <5    |          | 2      |       | 84   |        | 730   |            | 7     | 6          | 22     | 8         | 150     |         | 870     |
| 12/16/96                                  | 2.5 <5    |          | 6      |       | 46   |        | 760   |            | 120   | 4          | 2.5 <5 | 11        | 10      | 150     | 850     |
| 03/18/97                                  | 6         |          | 6      |       | 30   |        | 600   |            | 120   | 3.6        | 6      | 7         | 6       | 110     | 800     |
| 05/28/97                                  | 2.5 <5    |          | 5      |       | 36   |        | 610   |            | 110   | 5          | 11     | 20        | 2.5 <5  | 110     | 720     |
| 06/04/97                                  |           |          |        |       |      |        |       |            |       | 0.5 <1     |        |           |         |         |         |
| 09/15/97                                  | 2.5 <5    |          | 2      |       | 81   |        | 700   |            | 99    | 7          | 8      | 19        | 7       | 150     | 800     |
| 11/24/97                                  | 2.5 <5    |          | 4      |       | 310  |        | 770   |            | 120   | 4          | 15     | 33        | 6       | 160     | 880     |
| 02/02/98                                  | 3.4       | 4.1      |        | 120   |      | 780    |       | 120        | 4.1   | 13         | 25     | 6         | 140     | 810     |         |
| 08/04/98                                  | 4.6       | 5.3      |        | 39    |      | 921    | 117   | 4.6        | 13    | 14         | 6      | 123       |         |         | 829     |
| 11/24/98                                  | 5.5       | 3.1      |        | 33    |      | 770    | 94    | 3.91       | 7.8   | 18         |        | 6.3       | 120     |         | 860     |
| 12/22/98                                  | 5.5 <11   | 5.0      |        | 36    |      | 860    | 137   | 4.6        | 16    | 18 <11     |        | 5.5       | 130     |         | 930     |
| 03/23/99                                  | 4.9       | 4.2      |        | 30    |      | 699    | 98    | 3.1        | 22    | 14.7       |        | 6.3       | 119     |         | 909     |
| 06/29/99                                  | 1.65 <3.3 | 5.2      |        | 53    |      | 750    | 97    | 3.2        | 11    | 1.65 <3.3  |        | 1.65 <3.3 | 130     |         | 970     |
| 09/29/99                                  | 4.2       | 5.6      |        | 32    |      | 850    | 70    | 16         | 14    | 21         |        | 4.2       | 150     |         | 1060    |
| 12/15/99                                  | 1.7 <3.4  | 2.1 <4.2 |        | 47    |      | 690    | 14    | 6          | 14    | 17         |        | 4.2       | 140     |         | 710     |
| 03/30/00                                  | 3.5       | 4.3      |        | 28    |      | 670    | 77    | 3.83       | 11    | 14         |        | 4.3       | 130     |         | 700     |
| 06/19/00                                  | 3         | 1.9 <3.7 |        | 30    |      | 730    | 94    | 4.1        | 17    | 15         |        | 4.5       | 120     |         | 690     |
| 09/13/00                                  | 4.7       | 4.7      |        | 31    |      | 850    | 98.4  | 4          | 16.5  | 16         |        | 5.5       | 168     |         | 1110    |
| 10/02/00                                  | 4.8       | 4.0      | 4 <8.0 |       | 672  |        | 65.6  | 5.6        | 12.8  | 8          |        | 4.8       | 110     |         | 784     |
| 11/15/00                                  | 4.1       | 3.4      |        | 4     |      | 201    | 131   | 3.4        | 13.1  | 3          |        | 4.8       | 224     |         | 1570    |
| 02/26/01                                  | 2.9 <2.8  | 2.9      |        | 29    |      | 543    | 64.5  | 5.1        | 10.1  | 14         |        | 5.1       | 101     |         | 601     |
| 04/19/01                                  | 1.4 <2.8  | 1.7 <3.4 |        | 28    |      | 662    | 70.3  | 4.1        | 9     | 21         |        | 4.8       | 96.6    |         | 703     |
| 08/01/01                                  | 6.2       | 1.8 <3.5 |        | 28    |      | 690    | 71.1  | 2.1        | 13.8  | 14         |        | 6.2       | 91.8    |         | 732     |
| 10/11/01                                  | 6.3       | 1.8 <3.5 | 21     |       | 810  |        | 69.7  | 2.5        | 10.6  | 21         |        | 6.3       | 102     |         | 789     |
| 11/10/01                                  | 4.5       | 1.6 <3.2 |        | 26    |      | 708    | 69.5  | 4.5        | 9.7   | 13         |        | 3 <6.0    | 104     |         | 740     |
| 02/13/02                                  | 3         | 4.0      |        | 26    |      | 641    | 58    | 1.5 <3     | 5 <10 | 15 <30     |        | 4 <8      | 90      |         | 772     |
| 03/19/02                                  | 10 <20    | 10.0 <20 |        | 25    |      | 592    | 53    | 2          | 8     | 12         |        | 4.5 <9    | 76      |         | 638     |
| 04/17/02                                  | 6.1       | 3.0      |        | 20    |      | 600    | 55    | 4          | 9     | 12         |        | 4.6       | 87.2    |         | 645     |
| 05/16/02                                  | 3 <6      | 3.2      |        | 34    |      | 648    | 70    | 2.4        | 8.7   | 10 <20     |        | <         | 111     |         | 513     |
| Min                                       | 0.15      | 0.5      |        | 4     |      | 110    | 7.4   | 0.005      | 1     | 1.65       |        | 0.44      | 0.25    |         | 60      |
| Ave                                       | 3.48      | 3.87     |        | 47.73 |      | 671.33 | 88.17 | 3.61       | 12.78 | 15.85      |        | 4.62      | 108.06  |         | 1012.72 |
| Max                                       | 10        | 9.1      |        | 310   |      | 996    | 270   | 16         | 60.5  | 41.5       |        | 10        | 224     |         | 8850    |

# C. Ronan Montana Data

City of Ronan

All units are mg/L unless otherwise noted

| Cell  | Date          | BOD(in) | BOD(out) | % removal | TSS (in) | TSS(out) | % removal | pH (in) | pH (out) | greater than<br>org/100ml |                  | % removal | TP         | NO <sub>2</sub> /NO <sub>3</sub> | NH <sub>4</sub> <sup>+</sup> | TKN   |
|---|---------------|---------|----------|-----------|----------|----------|-----------|---------|----------|---------------------------|------------------|-----------|------------|----------------------------------|------------------------------|-------|
|   |               |         |          |           |          |          |           |         |          | Fecal Col. (in)           | Fecal Col. (out) |           |            |                                  |                              |       |
| Lagoons   | 1 1/10/1996   | 134     | 7        | 94.8      | 95       | 3        | 96.842    | 8.2     | 7.5      | 2.00E+05                  | 230              | 99.885    | 2.68       | 0.75                             | 9.18                         | 11.12 |
| Lagoons   | 2 2/14/1996   | 111     | 9        | 91.9      | 110      | 5        | 95.455    | 7.8     | 7.7      | 2.00E+05                  | 1760             | 99.12     | 2.25       | 0.02                             | 6.16                         | 7.45  |
| Lagoons   | 3 3/13/1996   | 92      | 16       | 82.6      | 130      | 13       | 90.000    | 7.8     | 7.8      | 2.00E+05                  | 80000            | 90        | 1.79       | 0.14                             | 4.41                         | 6.92  |
| Lagoons   | 4 4/3/1996    | 80      | 12       | 85.0      | 60       | 7        | 88.333    | 7.6     | 7.7      | 2.00E+05                  | 5800             | 97.1      | 2.09       | 0.01                             | 7.76                         | 10.8  |
| Mink Lane                                       | 5 5/9/1996    | 156     | 27       | 82.7      | 182      | 11       | 93.956    | 7.6     | 7.6      | 2.00E+05                  | 96               | 99.952    | 2.93       | 0.06                             | 11.35                        | 17.46 |
| Mink Lane                                       | 6 6/12/1996   | 157     | 24       | 84.7      | 92       | 18       | 80.435    | 7.6     | 7.4      | 2.00E+05                  | 460              | 99.77     | 2.96       | 0.08                             | 10.34                        | 15.89 |
| Lagoons   | 7 7/10/1996   | 167     | 40       | 76.0      | 110      | 46       | 58.182    | 7.4     | 8.6      | 2.00E+05                  | 100              | 100       | 2.83       | 2.86                             | 0.23                         | 5.65  |
| Mink Lane                                       | 8 7/10/1996   | 179     | 67       | 62.6      | 100      | 2        | 100.000   | 7.9     | 7.9      | 2.00E+05                  | 9500             | 95.25     | 3.15       | 0.11                             | 1.81                         | 6.97  |
| Lagoons   | 9 8/14/014    | 141     | 16       | 88.7      | 122      | 11       | 90.984    | 7.3     | 8.1      | 2.00E+05                  | 12               | 99.994    | 4.49       | 0.74                             | 1.72                         | 4.95  |
| 10 9/1/1996 NO DISCHARGE FOR MONTH OF SEPTEMBER |               |         |          |           |          |          |           |         |          |                           |                  |           |            |                                  |                              |       |
| 11 10/1/1996 NO DISCHARGE FOR MONTH OF OCTOBER  |               |         |          |           |          |          |           |         |          |                           |                  |           |            |                                  |                              |       |
| Lagoons #4                                      | 12 11/6/1996  | 92      | 22       | 76.1      | 32       | 20       | 37.500    | 7.5     | 7.9      | 2.00E+05                  | 62000            | 69        | 4.34       | 0.02                             | 10.51                        | 18.06 |
| Mink Lane                                       | 13 12/11/1996 | 169     | 8        | 95.3      | 144      | 16       | 88.889    | 7.6     | 7.8      | 2.00E+05                  | 48000            | 76        | 1.51       | 0.11                             | 3.71                         | 7.03  |
| Mink Lane                                       | 14 2/12/1997  | 179     | 14       | 92.2      | 159      | 3        | 98.113    | 7.6     | 7.6      | 2.00E+05                  | 390              | 99.805    | 2.16E+02   | 0.07                             | 10.18                        | 15.92 |
| Lagoon #2                                       | 15 2/13/1997  | 152     | 13       | 91.4      | 106      | 8        | 92.453    | 7.8     | 7.9      | 2.00E+05                  | 1400             | 99.3      | 2.41       | 0.14                             | 13.09                        | 19.86 |
| Mink Lane                                       | 16 3/6/1997   | 179     | 8        | 95.5      | 159      | 4        | 97.484    | 7.7     | 7.7      | 2.00E+05                  | 32               | 99.984    | 2.01       | 0.02                             | 8.51                         | 10.3  |
| Mink Lane                                       | 17 4/24/1997  | 179     | 8        | 95.5      | 159      | 2        | 100.000   |         |          | 2.00E+05                  | 560              | 99.72     |            |                                  |                              |       |
| Lagoon #2                                       | 18 4/18/1997  | 179     | 13       | 92.7      | 168      | 24       | 85.714    | 7.5     | 8.1      | 2.00E+05                  |                  |           | 2.54       | 0.03                             | 9.18                         | 15.88 |
| Mink Lane                                       | 19 5/15/1997  | 179     | 13       | 92.7      | 159      | 6        | 96.226    | 7.6     | 7.6      | 2.00E+05                  | 288              | 99.856    | 2.76       | 0.03                             | 9.12                         | 15.22 |
| Lagoons   | 20 5/15/1997  | 201     | 20       | 90.0      | 184      | 7        | 96.196    | 7.6     | 8.2      | 2.00E+05                  | 2300             | 98.85     | 2.76       | 0.13                             | 9.63                         | 17.32 |
| Mink Lane                                       | 21 6/12/1997  | 179     | 6        | 96.6      | 159      | 2        | 98.742    | 7.4     | 8.4      | 2.00E+05                  | 118              | 99.941    | 1.97       | 0.03                             | 6.46                         | 7.53  |
| Lagoons   | 22 6/12/1997  | 86      | 12       | 86.0      | 79       | 17       | 78.481    | 7.6     | 8.1      | 2.00E+05                  | 8                | 99.996    | 3.14       | 0.25                             | 11.38                        | 15.46 |
| Sewer/Lagoon                                    | 23 7/9/1997   | 114     | 11       | 90.4      | 100      | 2        | 98.000    | 7.2     | 8.1      | 2.00E+05                  | 1300             | 99.35     | 3.63       | 0.48                             | 16.23                        | 21.6  |
| Mink Lane                                       | 24 7/9/1997   | 179     | 8        | 95.5      | 159      | 10       | 93.711    | 7.7     | 7.7      | 2.00E+05                  | 5500             | 97.25     | 3.68       | 0.01                             | 15.55                        | 19.89 |
| Lagoons   | 25 8/20/1997  | 465     | 5        | 98.9      | 48       | 7        | 85.417    | 7.2     | 8        | 2.00E+05                  | 30               | 99.985    | 3.9 0.70   |                                  | 12.38                        | 18.69 |
| City of Ronan                                   | 26 10/8/1997  | 147     | 11       | 92.5      | 128      | 5        | 96.094    | 7.4     | 8.4      | 2.00E+05                  | 280              | 99.86     | 2.92       | 2.47                             | 5.67                         | 7.99  |
| City of Ronan                                   | 27 11/5/1997  | 146     | 11       | 92.5      | 106      | 12       | 88.679    | 7.5     | 8.8      | 2.00E+05                  | 10               | 99.995    | 2.8        | 3.43                             | 3.02                         | 6.48  |
| City of Ronan                                   | 28 12/11/1997 | 122     | 9        | 92.6      | 85       | 10       | 88.235    | 7.5     | 7.9      | 2.00E+05                  | 30               | 99.985    | 3.22       | 3.3                              | 7.48                         | 10.15 |
| Lagoons   | 29 1/15/1998  | 254     | 13       | 94.9      | 412      | 57       | 86.165    | 7.8     | 7.9      | 2.00E+05                  | 900              | 99.55     | 3.95       | 1.47                             | 13.98                        | 19.96 |
| Lagoons   | 30 2/5/1998   | 161     | 15       | 90.7      | 180      | 7        | 96.111    | 7.5     | 7.6      | 2.00E+05                  | 150000           | 25        | 3.83       | 1.06                             | 16.91                        | 22.33 |
| Lagoon #4                                       | 31 3/4/1998   | 146     | 13       | 91.1      | 208      | 12       | 94.231    | 7.7     | 8.5      | 2.00E+05                  | 2                | 99.999    | 2.98       | 1.37                             | 9.18                         | 15.05 |
| Lagoon #4                                       | 32 4/23/1998  | 179     | 23       | 87.2      | 159      | 13       | 91.824    |         | 8.6      | 2.00E+05                  | 12               | 99.994    | 3.5        | 1.4                              | 6.12                         | 12.11 |
| Lagoon #4                                       | 33 5/13/1998  | 179     | 15       | 91.6      | 159      | 39       | 75.472    | 7.8     | 7.8      | 2.00E+05                  | 200000           |           | 4.41       | 0.16                             | 10.39                        | 15.32 |
| Lagoons   | 34 6/18/1998  | 143     | 8        | 94.4      | 165      | 23       | 86.061    | 7.5     | 7.9      | 2.00E+05                  | 40               | 99.98     | 4.34       | 0.21                             | 18.34                        | 14.67 |
| Lagoon #4                                       | 35 7/9/1998   | 179     | 28       | 84.4      | 159      | 25       | 84.277    |         | 8        | 2.00E+05                  | 16800            | 91.6      | 2.94       | 1.18                             | 8.88                         | 10.38 |
| Lagoon #4                                       | 36 8/13/1998  | 179     | 5        | 97.2      | 159      | 6        | 96.226    |         | 7.9      | 2.00E+05                  | 76               | 99.962    | 2.85       | 0.04                             | 0.46                         | 2.37  |
| Lagoon #3                                       | 37 9/9/1998   | 179     | 4        | 97.8      | 159      | 9        | 94.340    |         | 8.1      | 2.00E+05                  | 106              | 99.947    | 3.26       | 1.7                              | 0.61                         | 2.44  |
| Lagoon #4                                       | 38 10/7/1998  | 179     | 1        | 99.4      | 159      | 1        | 99.371    |         | 7.6      | 2.00E+05                  | 12               | 99.994    | 1.92       | 0.06                             | 0.05                         | 0.97  |
| Lagoon #4                                       | 39 11/4/1998  | 179     | 2        | 98.9      | 159      | 2        | 98.742    |         | 7.6      | 2.00E+05                  | 42               | 99.979    | 2.1        | 0.08                             | 0.06                         | 1.46  |
| Lagoon #4                                       | 40 12/2/1998  | 179     | 6        | 96.6      | 159      | 25       | 84.277    |         | 7.8      | 2.00E+05                  | 16               | 99.992    | 2.46       | 1.17                             | 1.04                         | 3.34  |
| Lagoons #3                                      | 41 1/6/1999   | 165     | 24       | 85.5      | 246      | 57       | 76.929    |         | 7.9      | 2.00E+05                  | 900              | 99.55     | 3.95       | 1.47                             | 13.98                        | 19.96 |
| Lagoons #3                                      | 42 2/4/1999   | 224     | 18       | 92.0      | 212      | 17       | 91.981    | 7.4     | 7.6      | 2.00E+05                  | 1620             | 99.19     | 3.75       | 0.5                              | 18.03                        | 23.06 |
| Lagoons #4                                      | 43 3/3/1999   | 179     | 23       | 87.2      | 159      | 33       | 79.245    |         | 7.9      | 2.00E+05                  | 8                | 99.996    | 3.04       | 0.71                             | 12.6                         | 16.12 |
| Lagoon #1/#3                                    | 44 4/28/1999  | 190     | 30       | 84.2      | 328      | 44       | 86.585    | 7.6     | 8.5      | 2.00E+05                  | 430              | 99.785    | 3.76       | 2.03                             | 12.32                        | 17.8  |
| Lagoons #1/#3                                   | 45 5/5/1999   | 218     | 11       | 95.0      | 205      | 18       | 91.220    | 7.5     | 7.8      | 2.00E+05                  | 278              | 99.861    | 3.81       | 1.01                             | 14.82                        | 19.2  |
| Lagoon #4                                       | 46 6/3/1999   | 179     | 12       | 93.3      | 159      | 9        | 94.340    |         | 7.5      | 2.00E+05                  | 304              | 99.846    | 4.23       | 0.08                             | 8.16                         | 10.85 |
| Lagoon #4                                       | 47 7/8/1999   | 179     | 2        | 98.9      | 159      | 5        | 96.855    |         | 7.6      | 2.00E+05                  | 312              | 99.844    | 3.07       | 0.32                             | 1.29                         | 2.77  |
| Lagoon #4                                       | 48 8/18/1999  | 179     | 3        | 98.3      | 159      | 1        | 99.371    |         | 7.4      | 2.00E+05                  | 110000           | 45        | 4.34       | 0.04                             | 1.08                         | 2.85  |
| Lagoon #4                                       | 49 9/16/1999  | 179     | 9        | 95.0      | 159      | 6        | 96.226    |         | 7.4      | 2.00E+05                  | 3920             | 98.04     | 4.75       | 0.21                             | 2.09                         | 4.6   |
| Lagoon #4                                       | 50 10/7/1999  | 179     | 7        | 96.1      | 159      | 3        | 98.113    |         | 7.6      | 2.00E+05                  | 78               | 99.961    | 4.34       | 1.05                             | 0.62                         | 2.51  |
| Lagoon #4                                       | 51 11/17/1999 | 179     | 2        | 98.9      | 159      | 1        | 99.371    |         | 7.5      | 2.00E+05                  | 48               | 99.976    | 3.9        | 1.8                              | 4.13                         | 5.97  |
| Lagoon #1                                       | 52 12/8/1999  | 234     | 13       | 94.4      | 384      |          | 100.000   | 7.2     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #4                                       | 53 1/12/2000  | 179     | 5        | 97.2      | 159      | 5        | 96.855    |         | 7.5      | 2.00E+05                  | 58               | 99.971    | 3.63       | 2.85                             | 17.84                        | 18.5  |
| Lagoon #1                                       | 54 2/3/2000   | 206     | 13       | 93.7      | 178      |          | 100.000   | 7.3     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #4                                       | 55 3/9/2000   | 179     | 11       | 93.9      | 159      | 12       | 92.453    |         | 7.7      | 2.00E+05                  | 2                | 99.999    | 3.35       | 2.53                             | 15.6                         | 17.62 |
| Lagoon #4                                       | 56 4/19/2000  | 179     | 21       | 88.3      | 159      | 22       | 86.164    |         | 7.7      | 2.00E+05                  | 120              | 99.94     | 3.28       | 3.38                             | 5.08                         | 7.78  |
| Lagoon #1                                       | 57 5/11/2000  | 156     | 13       | 91.7      | 154      | 14       | 90.909    |         |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #1                                       | 58 6/14/2000  | 198     | 13       | 93.4      | 220      | 14       | 93.636    | 7.5     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #1                                       | 59 7/12/2000  | 202     | 13       | 93.6      | 198      | 14       | 92.929    | 7.5     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #1                                       | 60 8/10/2000  | 123     | 13       | 89.4      | 156      | 14       | 91.026    | 7.1     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #1                                       | 61 9/8/2000   | 580     | 13       | 97.8      | 164      | 14       | 91.463    | 7.2     |          | 2.00E+05                  |                  |           |            |                                  |                              |       |
| Lagoon #4                                       | 62 10/4/2000  | 179     | 3        | 98.3      | 159      | 4        | 97.484    |         | 7.4      | 2.00E+05                  | 188              | 99.906    | 3.83       | 0.99                             | 1.04                         | 2.8   |
| Lagoon #3                                       | 63 11/9/2000  | 179     | 22       | 87.7      | 159      | 35       | 77.987    |         | 8.3      | 2.00E+05                  | 1500             | 99.25     | 2.92       | 5.56 0.83                        |                              | 4.33  |
| Lagoon #3                                       | 64 12/7/2000  | 179     | 20       | 88.8      | 159      | 38       | 76.101    |         | 7.9      | 2.00E+05                  | 770              | 99.615    | 3.38       | 3.97                             | 5.27                         | 9.27  |
| Lagoon #4                                       | 65 1/11/2001  | 179     | 4        | 97.8      | 159      | 7        | 95.597    |         | 7.4      | 2.00E+05                  | 30               | 99.985    | 3.72       | 1.38                             | 12.53                        | 13.63 |
| Lagoon #4                                       | 66 2/21/2001  | 179     | 4        | 97.8      | 159      | 4        | 97.484    |         | 7.6      | 2.00E+05                  | 10               | 99.995    | 4.08       | 0.26                             | 21.38                        | 22.34 |
| Lagoon #4                                       | 67 3/22/2001  | 179     | 8        | 95.5      | 159      | 10       | 93.711    |         | 7.8      | 2.00E+05                  | 12               | 99.994    | 3.31       | 0.49                             | 17.37                        | 18.79 |
| Lagoon #4                                       | 68 4/26/2001  | 179     | 15       | 91.6      | 159      | 22       | 86.164    |         | 7.8      | 2.00E+05                  | 10               | 99.995    | 2.31       | 2.02                             | 0.54                         | 3.55  |
| Lagoon #4                                       | 69 5/3/2001   | 179     | 5        | 97.2      | 159      | 8        | 94.869    |         | 7.6      | 2.00E+05                  | 14               | 99.993    |            | 0.52                             |                              | 2.54  |
| 70 NO DATA FOR 6/2001                           |               |         |          |           |          |          |           |         |          |                           |                  |           |            |                                  |                              |       |
| Lagoon #3                                       | 71 7/11/2001  | 179     | 5        | 97.2      | 159      | 2        | 98.742    | 7.3     |          | 2.00E+05                  | 3000             | 98.5      | 4.01 <0.04 |                                  | 4.31                         | 5.68  |
| Lagoon #4                                       | 72 8/22/2001  | 179     | 3        | 98.3      | 159      | 1        | 99.371    | 8.1     |          | 2.00E+05                  | 336              | 99.832    | 4.73 <0.04 |                                  | 0.29                         | 1.78  |

## D. Seasonal Constructed Wetland Treatment Data

### Autumn

| Autumn Experimental Data       |            |       |       |       |       |       |       |         |        |          |              |       |       |
|--------------------------------|------------|-------|-------|-------|-------|-------|-------|---------|--------|----------|--------------|-------|-------|
| Date                           | Time (Hrs) | Time  | Temp  | pH    | COD   | TSS   | NH4   | NO3/NO2 | TDS    | Salinity | Conductivity | TKN   | BOD   |
| 10/8/2002                      | 0          | 8:15  | 16.7  | 7.102 | 304   | 65.00 | 20.69 | 0.01    | 489    | 0.5      | 977          | nr    | nr    |
| 10/15/2002                     | 0          | 8:15  | 16.7  | 7.252 | 272   | 56.00 | 21.95 | 0.01    | 516    | 0.5      | 1033         | nr    | nr    |
| 10/22/2002                     | 0          | 8:15  | 17.2  | 7.303 | 297   | 73.00 | 24.15 | 0.02    | 822    | 0.8      | 1642         | nr    | nr    |
| 11/12/2002                     | 0          | 8:50  | 15.7  | 7.350 | 278   | 49.00 | 23.35 | 0.02    | 706    | 0.7      | 1409         | nr    | nr    |
| 10/1/2002                      | 0          | 8:45  | 17.3  | 7.187 | 286   | 52.00 | 23.21 | 0.02    | 506    | 0.5      | 1014         | nr    | nr    |
| 9/9/2003                       | 0          | 11:00 | 20.3  | 7.551 | 297   | 88.71 | 40.86 | 0.21    | 592    | 0.6      | 1118         | 22.03 | 166.7 |
| 9/23/2003                      | 0          | 11:20 | 19.7  | 7.475 | 299   | 76.56 | 37.77 | 0.27    | 575    | 0.5      | 1085         | 54.67 | 231.0 |
| 9/30/2003                      | 0          | 11:00 | 19.6  | 7.589 | 303   | 64.00 | 40.91 | 0.26    | 593    | 0.6      | 1119         | 54.53 | 175.0 |
| 10/7/2003                      | 0          | 10:20 | 19.5  | 7.342 | 317   | 93.75 | 38.23 | 0.37    | 603    | 0.6      | 1138         | 50.39 | 171.7 |
| 10/14/2003                     | 0          | 11:10 | 18.9  | 7.551 | 320   | 79.17 | 39.92 | 0.03    | 580    | 0.5      | 1058         | 51.84 | 168.3 |
| 10/21/2003                     | 0          | 11:16 | 19.3  | 7.495 | 281   | 73.47 | 35.72 | 0.41    | 593    | 0.6      | 1118         | 49.01 | 163.3 |
| 11/4/2003                      | 0          | 10:00 | 14.6  | 7.411 | 439   | 75.51 | 35.17 | 0.44    | 549    | 0.5      | 1129         | 51.07 | 175.0 |
| 10/28/2003                     | 0          | 11:05 | 18.5  | 7.629 | 288   | 86.67 | 39.07 | 0.68    | 592    | 0.6      | 1116         | 57.50 | 160.0 |
|                                |            | Avg   | 18.0  | 7.4   | 306.2 | 71.8  | 32.4  | 0.2     | 593.5  | 0.6      | 1150.5       | 48.9  | 176.4 |
|                                |            | Stdev | 1.8   | 0.2   | 42.3  | 14.0  | 8.2   | 0.2     | 87.6   | 0.1      | 180.0        | 11.2  | 22.7  |
| 10/1/2002                      | 1          | 9:30  | 11.5  | 7.388 | 164   | 42.50 | 23.35 | 0.02    | 717    | 0.7      | 1434         | nr    | nr    |
| 10/1/2002                      | 2          | 10:30 | 9.4   | 7.279 | 140   | 29.20 | 16.56 | 0.04    | 435    | 0.4      | 867          | nr    | nr    |
| 11/12/2002                     | 3          | 11:00 | 10.1  | 7.302 | 160   | 46.20 | 20.88 | 0.04    | 773    | 0.8      | 843          | nr    | nr    |
| 11/12/2002                     | 4          | 12:00 | 9.5   | 7.302 | 151   | 40.00 | 18.76 | 0.01    | 659    | 0.6      | 1316         | nr    | nr    |
| 10/22/2002                     | 4          | 12:20 | 12.3  | 7.385 | 254   | 50.00 | 26.07 | 0.23    | 735    | 0.7      | 1468         | nr    | nr    |
| 10/15/2002                     | 4          | 12:00 | 15.8  | 7.496 | 256   | 76.00 | 30.15 | 0.06    | 760    | 0.8      | 1518         | nr    | nr    |
| 10/8/2002                      | 4          | 12:10 | 18.8  | 7.319 | 255   | 67.60 | 28.83 | 0.02    | 765    | 0.8      | 1528         | nr    | nr    |
| 10/28/2003                     | 5          | 4:00  | 16.8  | 7.358 | 294   | 74.00 | 31.69 | 0.20    | 551    | 0.5      | 1037         | 47.42 | nr    |
| 11/4/2003                      | 2          | 11:45 | 11.1  | 7.351 | 292   | 60.60 | 32.86 | 0.16    | 585    | 0.5      | 1103         | 48.80 | nr    |
| 10/21/2003                     | 6          | 5:20  | 19.8  | 7.259 | 306   | 69.39 | 29.88 | 0.01    | 566    | 0.5      | 1047         | 41.15 | nr    |
| 10/14/2003                     | 6          | 5:30  | 15.8  | 7.255 | 279   | 48.94 | 35.79 | 0.02    | 574    | 0.5      | 1071         | 43.66 | nr    |
| 10/7/2003                      | 7          | 5:20  | 19.1  | 7.274 | 296   | 54.17 | 31.99 | 0.00    | 579    | 0.5      | 1088         | 45.82 | nr    |
| 9/30/2003                      | 6          | 5:35  | 19.8  | 7.246 | 268   | 54.00 | 32.52 | 0.06    | 1      | 0.6      | 118          | 45.74 | nr    |
| 9/23/2003                      | 5          | 4:15  | 20.1  | 7.245 | 282   | 40.26 | 31.45 | 0.04    | 587    | 0.5      | 1104         | 45.03 | nr    |
| 9/9/2003                       | 5          | 5:30  | 19.7  | 7.346 | 250   | 55.36 | 34.15 | 0.01    | 580    | 0.5      | 1093         | 19.10 | nr    |
|                                |            | Avg   | 15.3  | 7.3   | 243.1 | 53.9  | 28.3  | 0.1     | 590.4  | 0.6      | 1089.0       | 42.1  | nr    |
|                                |            | Stdev | 4.2   | 0.1   | 58.5  | 13.6  | 5.9   | 0.1     | 190.8  | 0.1      | 376.7        | 9.6   | nr    |
| 10/9/2002                      | 24.5       | 8:30  | 10.8  | 7.252 | 86    | 14.60 | 5.42  | 0.01    | nr     | nr       | nr           | nr    | nr    |
| 10/2/2002                      | 25         | 9:30  | 7.3   | 7.261 | 47    | 5.00  | 2.41  | 0.09    | nr     | nr       | nr           | nr    | nr    |
| 11/13/2002                     | 26         | 10:00 | 7.5   | 7.127 | 72    | 18.00 | 9.83  | 0.01    | 611    | 0.6      | 1222         | nr    | nr    |
| 10/16/2002                     | 26.5       | 10:30 | 7.5   | 7.125 | 58    | 14.00 | 6.03  | 0.38    | 430    | nr       | 858          | nr    | nr    |
| 9/10/2003                      | 24         | 7:50  | 15.5  | 7.141 | 53    | 1.69  | 7.04  | 0.02    | 775    | 0.7      | 1455         | 9.95  | nr    |
| 9/24/2003                      | 24         | 7:50  | 13.3  | 7.308 | 112   | 17.54 | 14.70 | 0.02    | 689    | 0.6      | 1294         | 19.62 | nr    |
| 10/1/2003                      | 24         | 7:45  | 12.9  | 7.027 | 52    | 7.62  | 10.92 | 0.03    | 895    | 0.8      | 1687         | 14.38 | nr    |
| 10/8/2003                      | 24         | 7:45  | 13.7  | 7.223 | 75    | 7.02  | 9.14  | 0.02    | 894    | 0.8      | 1681         | 12.42 | nr    |
| 10/15/2003                     | 24         | 7:45  | 9.8   | 7.305 | 76    | 15.65 | 11.97 | 0.04    | 663    | 0.6      | 1242         | 15.12 | nr    |
| 10/22/2003                     | 24         | 8:00  | 12.9  | 7.237 | 90    | 6.00  | 11.97 | 0.01    | 613    | 0.6      | 11581        | 15.58 | nr    |
| 11/5/2003                      | 24         | 7:45  | 3.3   | 7.242 | 64    | 15.79 | 15.37 | 0.03    | 635    | 0.6      | 1195         | 19.34 | nr    |
| 10/29/2003                     | 24         | 7:45  | 8.1   | 7.039 | 58    | 7.34  | 5.49  | 0.06    | 709    | 0.7      | 1334         | 8.06  | nr    |
|                                |            | Avg   | 10.2  | 7.2   | 70.3  | 10.9  | 9.2   | 0.1     | 691.4  | 0.7      | 2354.9       | 14.3  | nr    |
|                                |            | Stdev | 3.6   | 0.1   | 19.0  | 5.6   | 4.0   | 0.1     | 139.3  | 0.1      | 3250.8       | 4.1   | nr    |
| 11/14/2002                     | 48         | 8:00  | 6.9   | 7.178 | 96    | 17.80 | 9.33  | 0.02    | 409    | 0.4      | 819          | nr    | nr    |
| 10/24/2002                     | 48         | 8:00  | 2.5   | 7.250 | 91    | 9.33  | 7.01  | 0.23    | 467    | 0.4      | 933          | nr    | nr    |
| 10/17/2002                     | 48         | 8:00  | 7.0   | 7.240 | 124   | 12.00 | 5.61  | 0.37    | 431    | 0.4      | 860          | nr    | nr    |
| 10/10/2002                     | 48         | 8:00  | 9.5   | 7.130 | 45    | 7.27  | 4.58  | 0.05    | 392    | 0.4      | 779          | nr    | nr    |
| 10/30/2003                     | 48         | 7:45  | 6.8   | 7.270 | 47    | 16.07 | 10.11 | 0.05    | 632    | 0.6      | 1187         | 13.34 | nr    |
| 11/6/2003                      | 48         | 7:45  | 1.8   | 7.257 | 68    | 10.45 | 16.66 | 0.01    | 654    | 0.6      | 1230         | 21.13 | nr    |
| 10/23/2003                     | 48         | 7:45  | 12.5  | 7.169 | 70    | 10.90 | 10.03 | 0.01    | 618    | 0.6      | 1158         | 13.17 | nr    |
| 10/16/2003                     | 48         | 7:45  | 9.7   | 7.237 | 55    | 0.17  | 9.04  | 0.08    | 666    | 0.6      | 1251         | 11.67 | nr    |
| 10/9/2003                      | 48         | 7:45  | 13.1  | 7.172 | 47    | 1.64  | 7.25  | 0.06    | 700    | 0.7      | 1317         | 9.30  | nr    |
| 10/2/2003                      | 48         | 7:45  | 12.9  | 7.238 | 66    | 4.84  | 9.86  | 0.06    | 723    | 0.7      | 1362         | 12.30 | nr    |
| 9/25/2003                      | 48         | 7:45  | 13.5  | 7.246 | 142   | 3.45  | 12.30 | 0.03    | 711    | 0.7      | 1335         | 16.42 | nr    |
| 9/11/2003                      | 48         | 7:45  | 15.5  | 7.080 | 12    | 1.72  | 8.46  | 0.04    | 750    | 0.7      | 1410         | 10.45 | nr    |
|                                |            | Avg   | 9.3   | 7.2   | 71.9  | 8.0   | 9.2   | 0.1     | 596.1  | 0.6      | 1136.8       | 13.5  | nr    |
|                                |            | Stdev | 4.4   | 0.1   | 36.3  | 5.8   | 3.2   | 0.1     | 132.9  | 0.1      | 227.4        | 3.8   | nr    |
| 10/8/2002                      | 167        | 8:00  | 10.2  | 7.021 | 86    | 7.69  | 0.47  | 0.14    | 337    | 0.3      | 672          | nr    | nr    |
| 10/15/2002                     | 168        | 8:00  | 6.9   | 7.172 | 42    | 1.00  | 1.53  | 0.71    | 396    | 0.4      | 790          | nr    | nr    |
| 10/22/2002                     | 168        | 8:00  | 7.3   | 7.162 | 49    | 3.29  | 1.60  | 1.47    | 427    | 0.4      | 853          | nr    | nr    |
| 10/29/2002                     | 168        | 8:00  | 0.8   | 7.108 | 55    | 6.67  | 4.57  | 0.45    | 500    | 0.5      | 1000         | nr    | nr    |
| 11/19/2002                     | 168        | 8:00  | 7.2   | 7.232 | 43    | 5.92  | 8.27  | 0.07    | 416    | 0.4      | 829          | nr    | nr    |
| 9/16/2003                      | 168        | 7:45  | 14.0  | 7.168 | 65    | 1.80  | 3.92  | 0.04    | 778    | 0.7      | 1468         | 7.38  | 10.6  |
| 9/30/2003                      | 168        | 7:45  | 12.0  | 7.093 | 58    | 3.70  | 3.19  | 0.18    | 779    | 0.7      | 1468         | 5.03  | 5.1   |
| 10/7/2003                      | 168        | 7:45  | 12.9  | 7.209 | 47    | 5.56  | 2.57  | 0.88    | 749    | 0.7      | 1407         | 4.78  | 3.1   |
| 10/14/2003                     | 168        | 7:45  | 8.9   | 7.086 | 48    | 0.00  | 1.56  | 0.79    | 731    | 0.7      | 1380         | 3.30  | 2.1   |
| 10/21/2003                     | 168        | 7:45  | 11.5  | 7.166 | 38    | 1.87  | 2.12  | 1.04    | 666    | 0.6      | 1255         | 3.95  | 2.4   |
| 10/28/2003                     | 168        | 8:00  | 10.1  | 7.094 | 43    | 2.00  | 4.89  | 0.64    | 634    | 0.6      | 1192         | 5.02  | 4.1   |
| 11/11/2003                     | 168        | 7:45  | 6.7   | 7.118 | 63    | 0.00  | 14.46 | 0.02    | 671    | 0.6      | 1256         | 18.73 | 4.1   |
| 11/4/2003                      | 168        | 7:45  | 4.4   | 7.173 | 32    | 3.57  | 8.38  | 1.05    | 643    | 0.6      | 1211         | 10.11 | 5.3   |
|                                |            | Avg   | 9.1   | 6.875 | 47    | 3.94  | 4.58  | 0.85    | 612    | 0.570    | 1160         | 7.32  | 4.4   |
|                                |            | Stdev | 3.7   | 0.1   | 14.1  | 2.5   | 3.9   | 0.5     | 158.0  | 0.1      | 276.7        | 5.1   | 2.7   |
| 9/16/2003                      | 168        | 7:45  | 14.5  | 7.473 | 48    | 6.35  | 3.26  | 2.15    | 744    | 0.7      | 1402         | 6.92  | nr    |
| 9/30/2003                      | 168        | 7:45  | 12.3  | 7.358 | 58    | 5.56  | 3.65  | 1.50    | 748    | 0.7      | 1405         | 5.67  | nr    |
| 10/7/2003                      | 168        | 7:45  | 13.2  | 7.295 | 46    | 4.76  | 2.88  | 1.40    | 737    | 0.7      | 1388         | 4.93  | nr    |
| 10/14/2003                     | 168        | 7:45  | 10.0  | 7.249 | 34    | 6.52  | 1.46  | 1.47    | 726    | 0.7      | 1361         | 3.72  | nr    |
| 10/21/2003                     | 168        | 7:45  | 12.0  | 7.264 | 33    | 3.45  | 2.25  | 1.45    | 662    | 0.6      | 1247         | 4.99  | nr    |
| 10/28/2003                     | 168        | 8:00  | 9.6   | 7.237 | 37    | 2.00  | 3.39  | 1.61    | 646    | 0.6      | 1199         | 5.51  | nr    |
| 11/11/2003                     | 168        | 7:45  | 6.6   | 7.214 | 51    | 5.26  | 14.15 | 0.01    | 662    | 0.6      | 1244         | 19.08 | nr    |
| 11/4/2003                      | 168        | 7:45  | 5.0   | 7.297 | 39    | 7.14  | 8.26  | 1.28    | 646    | 0.6      | 1218         | 10.24 | nr    |
|                                |            | Avg   | 10.40 | 7.30  | 43.25 | 5.13  | 3.59  | 1.36    | 696.38 | 0.65     | 1308.00      | 7.63  | nr    |
|                                |            | Stdev | 3.28  | 0.08  | 8.91  | 1.71  | 4.25  | 0.60    | 46.14  | 0.05     | 88.84        | 5.02  | nr    |
| Cell # 3 Internal Wetland Data |            |       |       |       |       |       |       |         |        |          |              |       |       |
| 9/11/2003                      | 48         | 7:45  | 15.9  | 7.378 | 17    | 9.80  | 12.54 | 0.09    | 682    | 0.6      | 1284         | 15.32 | nr    |
| 9/25/2003                      | 48         | 7:45  | 14.1  | 7.360 | 78    | 13.08 | 12.12 | 0.01    | 694    | 0.7      | 1304         | 15.98 | nr    |
| 10/2/20030                     |            |       |       |       |       |       |       |         |        |          |              |       |       |

## Winter

| Winter Experimental Data |      |          |      |       |      |        |       |       |       |     |       |       |       | Date | Time (Hrs) | Time | Temp | pH | COD | TSS | NH4 | NO3/NO2 | TDS | Salinity | Conductivity | TKN | BOD |
|--------------------------|------|----------|------|-------|------|--------|-------|-------|-------|-----|-------|-------|-------|------|------------|------|------|----|-----|-----|-----|---------|-----|----------|--------------|-----|-----|
| 2/24/2004                | 0    | 9:30     | 11.5 | 7.280 | 332  | 77.50  | 21.47 | 0.431 | 521   | 0.5 | 973   |       | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/10/2004                | 0    | 9:45     | 11.9 | 7.539 | 427  | 46.43  | 26.42 | 0.690 | 589   | 0.5 | 1111  |       | 37.34 | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 0    | 7:50 AM  | 9.0  | 7.245 | 318  | 63.56  | 22.87 | 0.020 | nr    | nr  | nr    | nr    | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 0    | 8:40 AM  | 8.6  | 7.327 | 316  | 61.00  | 23.40 | 0.020 | nr    | nr  | nr    | nr    | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/12/2002                | 0    | 7:45 AM  | 2.8  | 7.849 | 133  | 29.50  | 9.38  | 0.980 | nr    | nr  | nr    | nr    | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/19/2002               | 0    | 8:20     | 14.9 | 7.463 | 286  | 60.80  | 23.37 | 0.020 | 522   | 0.5 | 1038  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/26/2002               | 0    | 10:40    | 13.9 | 7.508 | 297  | 68.30  | 16.67 | 0.020 | 750   | 0.7 | 1498  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/3/2002                | 0    | 8:30     | 13.9 | 7.306 | 287  | 70.00  | 21.80 | 0.020 | 690   | 0.7 | 1379  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 1/30/2003                | 0    | 8:15     | 3.5  | 7.161 | 47   | 3.30   | 4.74  | 0.120 | 609   | 0.6 | 1218  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 1/30/2003                | 0    | 9:00     | 12.4 | 7.097 | 321  | 77.90  | 23.55 | 0.020 | 685   | 0.7 | 1369  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/6/2003                 | 0    | 7:45     | 11.4 | 7.249 | 349  | 74.50  | 24.39 | 0.020 | 495   | 0.5 | 984   |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/13/2003                | 0    | 8:30     | 11.5 | 7.252 | 318  | 73.00  | 26.33 | 0.030 | 669   | 0.7 | 1336  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/27/2003                | 0    | 10:00    | 11.3 | 7.682 | 292  | 82.00  | 34.30 | 0.140 | 772   | 0.8 | 1540  |       | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/11/2003               | 0    | 10:00    | 16.5 | 7.370 | 247  | 56.25  | 30.07 | 0.450 | 886   | 0.8 | 1670  | 42.49 | 146.7 |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/2/2003                | 0    | 11:10    | 15.5 | 7.620 | 400  | 102.20 | 39.11 | 0.330 | 589   | 0.5 | 1109  | 56.31 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/16/2003               | 0    | 10:40    | 14.3 | 7.606 | 289  | 88.09  | 38.24 | 0.760 | 617   | 0.6 | 1164  | 51.61 | 150.0 |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/9/2003                | 0    | 3:40     | 15.0 | 7.582 | 333  | 84.54  | 37.60 | 0.420 | 544   | 0.5 | 1025  | 57.56 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/25/2003               | 0    | 10:00    | 15.2 | 7.484 | 270  | 74.74  | 45.03 | 0.440 | 604   | 0.6 | 1136  | 50.97 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/18/2003               | 0    | 10:50    | 16.5 | 7.623 | 310  | 82.98  | 36.99 | 0.360 | 578   | 0.5 | 1089  | 54.08 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/13/2003                | 0    | 9:00     | 11.8 | 7.479 | 261  | 70.60  | 21.92 | 0.030 | 773   | 0.8 | 1549  | nr    | 175.0 |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 1    | 9:50 AM  | 8.5  | 7.481 | 300  | 66.00  | 22.51 | 0.020 | nr    | nr  | nr    | nr    | nr    | nr   |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Avg      | 15.1 | 7.438 | 292  | 70.49  | 32.43 | 0.267 | 641   | 0.6 | 1246  | 48.10 | 157.2 |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Stdev    | 3.8  | 0.2   | 80.1 | 21.2   | 9.8   | 0.3   | 107.0 | 0.1 | 220.6 | 8.8   | 15.5  |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/13/2003                | 2    | 10:20    | 5.3  | 7.363 | 110  | 29.80  | 16.59 | 0.080 | 642   | 0.6 | 1278  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/13/2003                | 2    | 11:00    | 10.7 | 7.408 | 132  | 30.40  | 13.57 | 0.670 | 740   | 0.7 | 1397  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/27/2003                | 2    | 11:40    | 3.3  | 7.456 | 159  | 46.10  | 18.01 | 0.940 | 720   | 0.7 | 1441  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/6/2003                 | 2    | 9:30     | 5.4  | 7.241 | 185  | 38.00  | 14.12 | 0.080 | 449   | 0.4 | 886   | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 1/30/2003                | 2    | 10:45    | 7.3  | 7.261 | 180  | 52.00  | 17.06 | 0.090 | 707   | 0.7 | 1412  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/3/2002                | 2    | 10:15    | 6.9  | 7.259 | 124  | 31.00  | 18.33 | 0.020 | 642   | 0.6 | 1281  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/26/2002               | 3    | 1:30     | 8.7  | 7.404 | 235  | 46.00  | 24.90 | 0.030 | 694   | 0.7 | 1388  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/3/2002                | 3    | 11:15    | 6.1  | 7.241 | 134  | 36.50  | 18.02 | 0.010 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/6/2003                 | 3    | 10:30    | 5.9  | 7.245 | 149  | 33.70  | 12.06 | 0.070 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/27/2003                | 3    | 12:40    | 3.3  | 7.462 | 114  | 28.40  | 12.24 | 1.090 | 658   | 0.6 | 1316  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/13/2003                | 3    | 12:00    | 12.1 | 7.448 | 103  | 27.50  | 12.74 | 0.680 | 606   | 0.6 | 1143  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 1/30/2003                | 3    | 11:45    | 7.1  | 7.226 | 187  | 38.00  | 15.83 | 0.070 | 665   | 0.7 | 1329  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 3    | 11:50 AM | 8.8  | 7.519 | 285  | 66.00  | 22.96 | 0.040 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/19/2002               | 3    | 11:00    | 10.5 | 7.383 | 147  | 40.40  | 18.63 | 0.040 | 690   | 0.7 | 1379  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/19/2002               | 4    | 12:00    | 10.8 | 7.360 | 132  | 98.00  | 17.77 | 0.020 | 626   | 0.6 | 1249  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/13/2003                | 4    | 11:20    | 5.4  | 7.349 | 119  | 24.50  | 14.31 | 0.070 | 625   | 0.6 | 1250  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 5.5  | 2:45 PM  | 9.3  | 7.692 | 262  | 66.00  | 21.12 | 0.050 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/14/2002                | 7.25 | 4:15 PM  | 8.7  | 7.769 | 242  | 65.00  | 21.21 | 0.040 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/18/2003               | 6    | 5:15     | 14.0 | 7.391 | 340  | 84.54  | 33.41 | 0.090 | 556   | 0.5 | 1048  | 47.90 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/25/2003               | 5    | 4:20     | 10.0 | 7.430 | 275  | 57.47  | 30.95 | 0.100 | 560   | 0.5 | 1055  | 43.90 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/9/2003                | 1    | 4:20     | 11.3 | 7.457 | 254  | 49.47  | 34.46 | 0.210 | 563   | 0.5 | 1059  | 50.33 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/16/2003               | 2    | 12:00    | 11.0 | 7.484 | 248  | 58.24  | 35.15 | 0.410 | 568   | 0.5 | 1070  | 45.51 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/2/2003                | 6    | 5:00     | 12.7 | 7.374 | nr   | 52.13  | 34.99 | 0.050 | 581   | 0.5 | 1094  | 48.79 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/11/2003               | 6    | 4:20     | 11.7 | 7.389 | 284  | 56.38  | 25.87 | 0.080 | 539   | 0.5 | 1010  | 41.10 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/10/2004                | 2    | 11:30    | 6.5  | 7.404 | 144  | 35.00  | 25.92 | 0.570 | 558   | 0.5 | 1052  | 38.03 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 2/24/2004                | 4    | 1:20     | 10.3 | 7.376 | 325  | 70.00  | 28.93 | 1.124 | 522   | 0.5 | 984   | 44.20 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Avg      | 8.6  | 7.400 | 195  | 48.48  | 21.51 | 0.259 | 615   | 0.6 | 1196  | 44.97 |       |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Stdev    | 2.9  | 0.1   | 73.1 | 18.6   | 7.6   | 0.4   | 74.5  | 0.1 | 166.6 | 4.1   |       |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/20/2002               | 24   | 8:20     | 8.8  | 7.192 | 72   | 12.00  | 9.79  | 0.020 | 435   | 0.4 | 868   | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/27/2002               | 25   | 11:20    | 3.3  | 7.277 | 120  | 17.00  | 14.88 | 0.030 | 488   | 0.5 | 981   | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/4/2002                | 25   | 9:20     | 3.5  | 7.239 | 75   | 18.00  | 14.88 | 0.010 | 518   | 0.5 | 1036  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/15/2002                | 25.5 | 10:20 AM | 5.7  | 7.135 | 228  | 50.50  | 20.50 | 0.020 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 1/31/2003                | 27.5 | 12:00    | 6.8  | 7.198 | 83   | 9.00   | 7.68  | 0.020 | 420   | 0.4 | 839   | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Avg      | 5.6  | 7.208 | 116  | 21.30  | 13.55 | 0.020 | 485   | 0.5 | 931   |       |       |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
|                          |      | Stdev    | 2.3  | 0.1   | 65.7 | 16.7   | 5.0   | 0.0   | 45.7  | 0.1 | 93.0  |       |       |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 3/15/2002                | 32.5 | 5:00 PM  | 7.1  | 7.151 | 212  | 57.00  | 18.86 | 0.020 | nr    | nr  | nr    | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/13/2003               | 48   | 7:45     | 6.8  | 7.136 | 112  | 10.71  | 18.48 | 0.030 | 621   | 0.6 | 1165  | 25.51 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/20/2003               | 48   | 7:45     | 6.6  | 7.107 | 103  | 16.39  | 22.28 | 0.000 | 598   | 0.6 | 1130  | 27.43 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/5/2002                | 48   | 8:20     | 3.4  | 7.154 | 76   | 14.70  | 14.72 | 0.010 | 513   | 0.5 | 1022  | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/21/2002               | 48   | 8:00     | 7.6  | 7.266 | 55   | 10.00  | 10.36 | 0.030 | 441   | 0.4 | 880   | nr    | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/4/2003                | 48   | 7:45     | 6.0  | 7.209 | 85   | 3.28   | 24.69 | 0.010 | 595   | 0.5 | 1115  | 28.21 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/27/2003               | 48   | 7:45     | 5.4  | 7.182 | 87   | 18.02  | 24.81 | 0.000 | 602   | 0.6 | 1133  | 27.93 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/18/2003               | 48   | 7:45     | 3.4  | 7.180 | 67   | 10.71  | 24.00 | 0.010 | 581   | 0.5 | 1093  | 26.45 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 12/11/2003               | 48   | 7:45     | 4.1  | 7.250 | 86   | 8.33   | 27.58 | 0.010 | 585   | 0.5 | 1103  | 32.38 | nr    |      |            |      |      |    |     |     |     |         |     |          |              |     |     |
| 11/28/2002               | 49   | 11:20    | 3.3  | 7.225 | 90   | 17.00  | 14.26 | 0.02  |       |     |       |       |       |      |            |      |      |    |     |     |     |         |     |          |              |     |     |

## Spring

| Spring Experimental Data |            |       |        |       |       |        |          |            |       |          |              |      |             |
|--------------------------|------------|-------|--------|-------|-------|--------|----------|------------|-------|----------|--------------|------|-------------|
| Date                     | Time (Hrs) | Time  | Temp   | pH    | COD   | TSS    | NH4      | NO3/NO2    | TDS   | Salinity | Conductivity | TKN  | BOD         |
| 6/4/2002                 | 0          | 12:00 | 15.1   | 7.695 | 421   | 47.30  | 15.74    |            | 474   | 0.5      | 949          | nr   | nr          |
| 4/3/2003                 | 0          | 7:45  | 6.3    | 7.260 | 152   | 77.00  | 0.08     | 0.07       | 386   | 0.3      | 723          | nr   | nr          |
| 4/3/2003                 | 0          | 9:15  | 12.4   | 7.495 | 294   | 82.90  | 23.73    | 0.07       | 703   | 0.7      | 1325         | nr   | nr          |
| 4/10/2003                | 0          | 7:50  | 7.4    | 7.266 | 62    | 7.30   | 0.23     | 0.13       | 406   | 0.4      | 765          | nr   | nr          |
| 4/10/2003                | 0          | 7:50  | 7.2    | 7.339 | 65    | 7.30   | 0.12     | 0.24       | 405   | 0.4      | 763          | nr   | nr          |
| 4/17/2003                | 0          | 10:00 | 12.9   | 7.567 | 255   | 58.50  | 28.05    | 0.15       | 840   | 0.8      | 1583         | nr   | 105         |
| 4/29/2003                | 0          | 7:50  | 7.8    | 7.270 | 85    | 24.50  | 0.09     | 0          | 448   | 0.4      | 845          | nr   | 9.6         |
| 5/10/2003                | 0          | 10:30 | 8.9    | 7.096 | 114   | 40.80  | 0.03     | 0.03       | 439   | 0.4      | 828          | nr   | nr          |
| 5/14/2003                | 0          | 8:10  | 9.9    | 6.963 | 98    | 46.40  | 0.33     | 0.08       | 450   | 0.4      | 849          | 4.27 | 12.2        |
| 5/14/2003                | 0          | 10:50 | 16.3   | 7.666 | 295   | 104.40 | 36.19    | 0.15       | 622   | 0.6      | 1172         | nr   | 150         |
|                          |            | Avg   | 14.1   | 7.6   | 310   | 80.269 | 29.905   | 0.11166667 | 659.2 | 0.633333 | 1243.333333  |      | 143.3333333 |
|                          |            | Stdev | 3.5348 | 0.241 | 123.7 | 32.048 | 14.19571 | 0.07293452 | 152.4 | 0.159513 | 286.4168679  |      | 69.78882432 |
| 4/17/2003                | 0.3        | 10:20 | 9.9    | 7.354 | 147   | 37.50  | 9.87     | 0.05       | 600   | 0.6      | 1132         | nr   | nr          |
| 5/10/2003                | 0.75       | 12:00 | 15.6   | 7.805 | 305   | 85.70  | 36.54    | 0.15       | 601   | 0.6      | 1137         | nr   | nr          |
| 4/10/2003                | 1          | 9:20  | 12.6   | 7.275 | 329   | 91.18  | 23.65    | 0.02       | 572   | 0.5      | 1079         | nr   | nr          |
| 4/17/2003                | 1.3        | 11:20 | 11.2   | 7.368 | 125   | 28.40  | 8.71     | 0.05       | 629   | 0.6      | 1188         | nr   | nr          |
| 4/29/2003                | 1.6        | 10:00 | 13.8   | 7.699 | 271   | 91.90  | 31.27    | 0.13       | 617   | 0.6      | 1164         | nr   | 175         |
| 6/4/2002                 | 3          | 3:00  | 16.7   | 7.492 | 415   | 53.00  | 16.53    | nr         | 485   | 0.5      | 971          | nr   | nr          |
| 4/3/2003                 | 2          | 11:00 | 9      | 7.562 | 233   | 43.00  | 11.02    | 0.05       | 732   | 0.7      | 1380         | nr   | nr          |
| 4/10/2003                | 2          | 10:15 | 10.3   | 7.378 | 210   | 53.92  | 12.81    | 0.07       | 639   | 0.6      | 1204         | nr   | nr          |
| 5/10/2003                | 2          | 1:20  | 13.9   | 7.519 | 190   | 76.10  | 14.3     | 0.08       | 502   | 0.5      | 946          | nr   | nr          |
| 5/14/2003                | 2.3        | 11:30 | 15.3   | 7.323 | 195   | 60.14  | 17.59    | 0.08       | 535   | 0.5      | 1007         | nr   | nr          |
| 4/3/2003                 | 3          | 12:00 | 8.8    | 7.623 | 154   | 43.30  | 10.06    | 0.06       | 633   | 0.6      | 1193         | nr   | nr          |
| 4/10/2003                | 3          | 11:15 | 11.4   | 6.624 | 172   | 42.00  | 10.47    | 0.05       | 840   | 0.8      | 1584         | nr   | nr          |
| 4/29/2003                | 4          | 12:40 | 12.1   | 6.630 | 225   | 62.20  | 20.78    | 0.06       | 564   | 0.5      | 1062         | nr   | nr          |
|                          |            | Avg   | 11.86  | 7.287 | 206.6 | 49.956 | 13.214   | 0.06111111 | 615.9 | 0.59     | 1166.7       |      |             |
|                          |            | Stdev | 2.567  | 0.359 | 82.47 | 21.187 | 8.732012 | 0.03629634 | 94.07 | 0.089872 | 171.8335509  |      |             |
| 6/5/2002                 | 20         | 8:20  | 15.2   | 7.568 | 432   | 58.70  | 11.26    | nr         | 483   | 0.5      | 965          | nr   | nr          |
| 4/4/2003                 | 23         | 8:10  | 5.8    | 7.297 | 96    | 17.60  | 2.24     | 0.26       | 406   | 0.4      | 765          | nr   | nr          |
| 4/11/2003                | 24.25      | 8:00  | 10.1   | 6.437 | 82    | 29.00  | 2.2      | 0.08       | 460   | 0.4      | 866          | nr   | nr          |
| 4/18/2003                | 24         | 9:20  | 8.8    | 7.287 | 84    | 21.30  | 1.22     | 0.12       | 423   | 0.4      | 797          | nr   | nr          |
| 4/30/2003                | 24.3       | 9:00  | 9.1    | 7     | 121   | 30.20  | 4.87     | 0.02       | 467   | 0.4      | 881          | nr   | nr          |
|                          |            | Avg   | 9.8    | 7.16  | 95.75 | 24.525 | 2.6325   | 0.12       | 439   | 0.4      | 827.25       |      |             |
|                          |            | Stdev | 3.4183 | 0.426 | 151.2 | 16.163 | 4.089306 | 0.10198039 | 32.09 | 0.044721 | 78.03973347  |      |             |
| 4/20/2003                | 36         | 12:00 | 10.3   | 7.260 | 88    | 41.50  | 0.21     | 0.06       | 426   | 0.4      | 803          | nr   | nr          |
|                          |            |       | 10.3   | 7.260 | 88    | 41.50  | 0.21     | 0.06       | 426   | 0.4      | 803          |      |             |
| 5/1/2003                 | 48         | 8:30  | 10.2   | 7.157 | 112   | 29.40  | 3.21     | 0.09       | 715   | 0.7      | 1347         | nr   | nr          |
|                          |            |       | 10.2   | 7.157 | 112   | 29.40  | 3.21     | 0.09       | 715   | 0.7      | 1347         |      |             |
| 6/7/2002                 | 68         | 8:30  | 12.1   | 7.073 | 238   | 68.00  | 7.54     |            | 488   | 0.5      | 975          | nr   | nr          |
| 4/13/2003                | 75.25      | 11:30 | 11.2   | 7.409 | 81    | 18.87  | 0.58     | 0.04       | 410   | 0.4      | 773          | nr   | nr          |
|                          |            | Avg   | 11.2   | 7.409 | 81    | 18.87  | 0.58     | 0.04       | 410   | 0.4      | 773          |      |             |
|                          |            | Stdev | 0.6364 | 0.238 | 111   | 34.74  | 4.921463 | #DIV/0!    | 55.15 | 0.070711 | 142.8355698  |      |             |
| 5/14/2003                | 96         | 8:10  | 9.9    | 6.963 | 98    | 46.40  | 0.44     | 0.08       | 450   | 0.4      | 849          | 4.27 | 12.2        |
| 4/22/2003                | 120        | 7:45  | 11.4   | 7.186 | 67    | 13.00  | 0.17     | 0.03       | 427   | 0.4      | 807          | nr   | nr          |
| 4/8/2003                 | 128        | 5:30  | 11.2   | 7.335 | 85    | 19.30  | 0.08     | 0.58       | 575   | 0.5      | 1085         | nr   | nr          |
|                          |            | Avg   | 10.833 | 7.161 | 83.33 | 26.233 | 0.23     | 0.23       | 484   | 0.433333 | 913.6666667  | 4.27 | 12.2        |
|                          |            | Stdev | 0.8145 | 0.187 | 15.57 | 17.747 | 0.18735  | 0.30413813 | 79.64 | 0.057735 | 149.8577103  |      |             |
| 6/12/2002                | 188        | 8:30  | 10.9   | 7.670 | 448   | 10.50  | 2.94     |            | 427   | 0.4      | 853          | nr   | nr          |
| 4/10/2003                | 167        | 7:50  | 7.4    | 7.266 | 62    | 7.30   | 0.23     | 0.13       | 406   | 0.4      | 765          | nr   | nr          |
| 4/17/2003                | 167.75     | 7:50  | 7.7    | 7.213 | 67    | 46.70  | 0.13     | 0.1        | 667   | 0.6      | 1258         | nr   | 7.8         |
| 4/24/2003                | 168        | 7:15  | 11.2   | 7.169 | 90    | 7.30   | 0.67     | 0.03       | 432   | 0.4      | 813          | nr   | nr          |
| 5/20/2003                | 168        | 8:10  | 8.1    | 7.000 | 123   | 30.00  | 0.32     | 0.07       | 460   | 0.4      | 868          | 5.93 | 20.2        |
|                          |            | Avg   | 8.6    | 7.162 | 85.5  | 22.825 | 0.3375   | 0.0825     | 491.3 | 0.45     | 926          | 5.93 | 14          |
|                          |            | Stdev | 1.8366 | 0.248 | 163.9 | 17.501 | 1.181512 | 0.04272002 | 107.2 | 0.089443 | 197.8264391  |      | 9           |



# Summer

| Summer Experimental Data |     |       |      |       |     |        |        |       |     |     |      |       |       |  | Date | Time (Hrs) | Time  | Temp  | pH    | COD  | TSS   | NH4 | NO3/NO2 | TDS   | Salinity | Conductivity | TKN | BOD |
|--------------------------|-----|-------|------|-------|-----|--------|--------|-------|-----|-----|------|-------|-------|--|------|------------|-------|-------|-------|------|-------|-----|---------|-------|----------|--------------|-----|-----|
| 7/2/2002                 | 0   | 8:00  | 16.1 | 6.667 | 425 | 52.00  | 7.47   | 0.04  | 488 | 0.5 | 974  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/3/2002                 | 0   | 8:00  | 16.3 | 6.999 | 321 | 39.60  | 16.93  | 0.03  | 454 | 0.4 | 909  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/4/2002                 | 0   | 12:00 | 15.1 | 7.695 | 421 | 47.30  | 15.74  |       | 474 | 0.5 | 949  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/10/2003                | 0   | 10:40 | 18.4 | 7.529 | 262 | 88.16  | 27.58  | 0.07  | nr  | nr  | nr   | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/17/2003                | 0   | 12:45 | 19.2 | 7.493 | 480 | 92.00  | 34.25  | 0.17  | 502 | 0.5 | 945  | 46.55 | 133.8 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/24/2003                | 0   | 10:00 | 18.1 | 7.444 | 188 | 54.80  | 31.94  | 0.03  | 569 | 0.5 | 1076 | 31.04 | 165   |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/1/2003                 | 0   | 10:00 | 18.7 | 7.463 | 243 | 66.70  | 31.86  | 0.06  | 601 | 0.6 | 1132 | 40.16 | 118.3 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/8/2003                 | 0   | 10:00 | 18.2 | 7.263 | 286 | 73.70  | 29.008 | 0.014 | 547 | 0.5 | 1036 | 38.95 | 113.3 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/15/2003                | 0   | 10:05 | 19.1 | 7.471 | 217 | 61.00  | 37.373 | 0.015 | 621 | 0.6 | 1170 | 49.85 | 105   |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/22/2003                | 0   | 10:10 | 19.5 | 7.524 | 204 | 50.90  | 36.79  | 0.03  | 640 | 0.6 | 1210 | 48.69 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/29/2003                | 0   | 10:30 | 20.1 | 7.258 | 231 | 59.60  | 25.76  | 0.00  | 588 | 0.5 | 1115 | 33.19 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/5/2003                 | 0   | 10:30 | 20.3 | 7.247 | 215 | 60.30  | 34.43  | 0.01  | 627 | 0.6 | 1186 | 41.94 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/12/2003                | 0   | 10:00 | 19.3 | 7.237 | 241 | 56.30  | 26.05  | 0.03  | 542 | 0.5 | 1021 | 38.33 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/19/2003                | 0   | 10:00 | 20.3 | 7.221 | 333 | 61.50  | 29.70  | 0.09  | 596 | 0.6 | 1134 | 41.82 | 141.7 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/26/2003                | 0   | 10:00 | 20.4 | 7.170 | 293 | 85.19  | 34.47  | 0.05  | 608 | 0.6 | 1144 | 42.11 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 9/2/2003                 | 0   | 9:53  | 19.9 | 7.354 | 213 | 43.59  | 29.15  | 0.08  | 593 | 0.6 | 1153 | 17.55 | 123.3 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/3/2003                 | 0   | 10:05 | 16.5 | 7.508 | 232 | 102.00 | 32.36  | 0.17  | 601 | 0.6 | 1132 | 46.67 | 116.7 |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 5/20/2003                | 0   | 10:30 | 15.3 | 7.484 | 309 | 89.20  | 31.24  | 0.03  | 617 | 0.6 | 1163 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| Avg                      |     |       |      |       |     |        |        |       |     |     |      |       |       |  | 18.4 | 7.3        | 284.1 | 65.8  | 31.5  | 0.1  | 568.7 | 0.5 | 1085.2  | 40.1  | 122.1    |              |     |     |
| Stdev                    |     |       |      |       |     |        |        |       |     |     |      |       |       |  | 1.8  | 0.2        | 84.4  | 18.4  | 7.9   | 0.1  | 57.6  | 0.1 | 94.5    | 8.5   | 23.5     |              |     |     |
| 5/20/2003                | 1   | 11:08 | 13.1 | 7.307 | 230 | 69.30  | 14.61  | 0.03  | 530 | 0.5 | 999  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/4/2002                 | 3   | 3:00  | 16.7 | 7.492 | 415 | 53.00  | 16.53  | nr    | 485 | 0.5 | 971  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/3/2003                 | 5.5 | 2:05  | 18.4 | 7.168 | 200 | 59.70  | 21.31  | 0.02  | 521 | 0.5 | 980  | 38.27 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/3/2003                 | 5.5 | 2:10  | 18.4 | 7.158 | 205 | 56.90  | 21.09  | 0.02  | 523 | 0.5 | 986  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/3/2002                 | 3   | 11:30 | 16.5 | 6.957 | 371 | 76.90  | 16.59  | 0.03  | 403 | 0.4 | 806  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/3/2002                 | 5   | 1:30  | 17.3 | 7.066 | 323 | 28.00  | 16.4   | 0.03  | 777 | 0.8 | 1555 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/3/2002                 | 6.5 | 3:00  | 18.5 | 6.859 | 290 | 34.00  | 16.9   | 0.01  | 422 | 0.4 | 843  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/29/2003                | 8.5 | 5:00  | 23.5 | 7.166 | 229 | 49.20  | 27.03  | 0.01  | 709 | 0.6 | 1339 | 34.56 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/29/2003                | 8.5 | 5:00  | 23.5 | 7.140 | 242 | 50.80  | 26.98  | 0.00  | 577 | 0.6 | 1090 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/19/2003                | 7   | 5:00  | 21.2 | 7.263 | 259 | 33.90  | 26.88  | 0.02  | 568 | 0.5 | 1074 | 38.63 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/26/2003                | 4   | 2:00  | 22.1 | 7.241 | 273 | 42.86  | 33.10  | 0.02  | 605 | 0.6 | 1144 | 44.24 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 9/2/2003                 | 7   | 4:10  | 21.8 | 7.208 | 317 | 44.79  | 29.34  | 0.02  | 546 | 0.5 | 1030 | 18.35 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/12/2003                | 7   | 4:40  | 20.4 | 7.198 | 278 | 29.60  | 25.43  | 0.02  | 610 | 0.6 | 1147 | 34.57 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/12/2003                | 7   | 4:40  | 20.2 | 7.163 | 235 | 24.20  | 25.65  | 0.03  | 608 | 0.6 | 1146 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/5/2003                 | 9   | 5:00  | 21.0 | 7.232 | 234 | 22.40  | 30.04  | 0.01  | 576 | 0.5 | 1086 | 37.4  | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/5/2003                 | 9   | 5:00  | 21.4 | 7.221 | 262 | 38.80  | 30.31  | 0.01  | 571 | 0.5 | 1076 | 37.46 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/22/2003                | 8.5 | 4:25  | 23.3 | 7.167 | 241 | 43.10  | 33.57  | 0.01  | 592 | 0.6 | 1124 | 42.77 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/22/2003                | 8.5 | 4:25  | 23.3 | 7.172 | 230 | 42.90  | 33.51  | 0.02  | 590 | 0.6 | 1111 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/15/2003                | 8   | 4:15  | 20.7 | 7.157 | 268 | 45.20  | 32.954 | 0.006 | 567 | 0.5 | 1071 | 44.53 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/15/2003                | 8   | 4:15  | 20.7 | 7.147 | 263 | 51.70  | 33.083 | 0.005 | 579 | 0.5 | 1097 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/8/2003                 | 9   | 5:30  | 21   | 7.115 | 248 | 48.70  | 28.219 | 0.013 | 526 | 0.5 | 993  | 38.7  | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/8/2003                 | 9   | 5:30  | 21   | 7.136 | 247 | 51.90  | 27.969 | 0.017 | 658 | 0.6 | 1226 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/1/2003                 | 7   | 3:30  | 19.2 | 7.111 | 272 | 50.90  | 29.16  | 0.01  | 539 | 0.5 | 1022 | 37.51 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/1/2003                 | 7   | 3:50  | 19.2 | 7.080 | 265 | 52.10  | 28.96  | 0.01  | 537 | 0.5 | 1014 | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/24/2003                | 7   | 3:00  | 19   | 7.097 | 196 | 47.50  | 24.47  | 0.01  | 511 | 0.5 | 967  | 24.47 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/24/2003                | 7   | 3:00  | 19   | 7.090 | 190 | 40.00  | 22.56  | 0.01  | 511 | 0.5 | 967  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/17/2003                | 6   | 3:30  | 19.2 | 7.139 | 237 | 51.70  | 25.6   | 0.03  | 528 | 0.5 | 998  | 33.8  | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/17/2003                | 6   | 3:30  | 19.2 | 7.085 | 227 | 44.40  | 24.38  | 0.02  | 522 | 0.5 | 986  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/10/2003                | 7.5 | 3:30  | 20.1 | 7.149 | 282 | 93.90  | 18.17  | 0.01  | nr  | nr  | nr   | 28.05 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/10/2003                | 7.5 | 3:30  | 20.1 | 7.149 | 273 | 62.12  | 17.27  | 0.02  | nr  | nr  | nr   | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| Avg                      |     |       |      |       |     |        |        |       |     |     |      |       |       |  | 20.0 | 7.154      | 260   | 48.02 | 25.27 | 0.02 | 560   | 0.5 | 1066    | 35.55 |          |              |     |     |
| Stdev                    |     |       |      |       |     |        |        |       |     |     |      |       |       |  | 2.3  | 0.1        | 48.5  | 15.0  | 5.9   | 0.0  | 74.9  | 0.1 | 143.0   | 7.2   |          |              |     |     |
| 7/4/2002                 | 26  | 9:30  | 17.9 | 6.824 | 335 | 56.90  | 16.2   | 0.03  | 438 | 0.4 | 880  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/4/2002                 | 30  | 1:30  | 19.2 | 6.764 | 301 | 49.00  | 16.83  | 0.02  | 439 | 0.4 | 883  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/5/2002                 | 20  | 8:20  | 15.2 | 7.568 | 432 | 58.70  | 11.26  | nr    | 483 | 0.5 | 965  | nr    | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/11/2003                | 24  | 9:30  | 16.7 | 6.818 | 103 | 21.21  | 4.97   | 0.02  | 479 | 0.4 | 904  | 10.53 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/18/2003                | 24  | 9:10  | 19.6 | 6.836 | 158 | 36.80  | 11.51  | 0.02  | 592 | 0.5 | 947  | 20.11 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 6/25/2003                | 24  | 8:20  | 15.1 | 7.753 | 126 | 13.60  | 10.83  | 0.01  | 495 | 0.5 | 931  | 24.14 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/2/2003                 | 24  | 8:10  | 18.1 | 6.742 | 194 | 29.10  | 10.30  | 0.00  | 505 | 0.5 | 951  | 16.52 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/9/2003                 | 24  | 8:30  | 18.1 | 6.818 | 144 | 21.90  | 14.601 | 0.012 | 524 | 0.5 | 989  | 21.44 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/16/2003                | 24  | 8:10  | 19.6 | 6.927 | 167 | 26.60  | 16.302 | 0.007 | 561 | 0.5 | 1057 | 26.15 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/23/2003                | 24  | 8:00  | 20   | 6.956 | 145 | 8.70   | 17.79  | 0.00  | 627 | 0.6 | 1187 | 22.94 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 7/30/2003                | 24  | 8:15  | 20.1 | 7.035 | 109 | 1.30   | 18.12  | 0.01  | 644 | 0.6 | 1216 | 22.44 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/27/2003                | 24  | 9:00  | 19.3 | 7.159 | 90  | 18.55  | 16.55  | 0.02  | 723 | 0.7 | 1361 | 19.14 | 5.75  |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 9/3/2003                 | 24  | 7:45  | 17.7 | 7.202 | 92  | 3.28   | 14.31  | 0.02  | 701 | 0.7 | 1321 | 16.73 | nr    |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |
| 8/13/2003                |     |       |      |       |     |        |        |       |     |     |      |       |       |  |      |            |       |       |       |      |       |     |         |       |          |              |     |     |

## E. XL Stat data for Autumn, Winter, Spring and Summer

### Autumn

|  |         |         |         |         |         |
|--|---------|---------|---------|---------|---------|
| Autumn Temperature   |         |         |         |         |         |
| XLSTAT 7.5.3 - Descriptive statistics - 9/10/2005 at 8:12:40 PM  |         |         |         |         |         |
| Quantitative data description  |         |         |         |         |         |
| Data: workbook = XLStat Practice.xls / sheet = Autumn by Hour / range = \$AF\$16:\$AJ\$30 / 15 rows and 5 columns                        |         |         |         |         |         |
| Missing values in <Data> were ignored  |         |         |         |         |         |
| Uniform weighting (default)  |         |         |         |         |         |
| Confidence interval (%): 90.00   |         |         |         |         |         |
|  | Hour    |         |         |         |         |
|  | 0       | 7       | 24      | 48      | 168     |
| No. of values used   | 13      | 15      | 12      | 12      | 13      |
| No. of values ignored  | 2       | 0       | 3       | 3       | 2       |
| No. of min. val.   | 1       | 1       | 1       | 1       | 1       |
| % of min. val.   | 7.692   | 6.667   | 8.333   | 8.333   | 7.692   |
| Minimum  | 14.600  | 9.400   | 3.300   | 1.800   | 0.800   |
| 1st quartile   | 16.700  | 11.100  | 7.500   | 6.850   | 6.800   |
| Median   | 18.500  | 15.800  | 10.300  | 9.600   | 8.910   |
| 3rd quartile   | 19.550  | 19.700  | 13.100  | 13.000  | 11.750  |
| Maximum  | 20.300  | 20.100  | 15.500  | 15.500  | 14.000  |
| Range  | 5.700   | 10.700  | 12.200  | 13.700  | 13.200  |
| Sum  | 234.000 | 229.600 | 122.600 | 111.700 | 112.900 |
| Mean   | 18.000  | 15.307  | 10.217  | 9.308   | 8.685   |
| Geometric mean   | 17.918  | 14.723  | 9.508   | 7.912   | 7.388   |
| Harmonic mean  | 17.833  | 14.122  | 8.618   | 6.088   | 4.858   |
| Kurtosis (Pearson)   | -1.233  | -1.783  | -1.144  | -1.304  | -0.632  |
| Skewness (Pearson)   | -0.412  | -0.198  | -0.270  | -0.327  | -0.468  |
| Kurtosis   | -0.761  | -1.763  | -0.524  | -0.826  | 0.317   |
| Skewness   | -0.528  | -0.245  | -0.354  | -0.429  | -0.599  |
| CV (standard deviation/mean)   | 0.098   | 0.275   | 0.349   | 0.474   | 0.422   |
| Sample variance  | 2.854   | 16.594  | 11.671  | 17.809  | 12.383  |
| Estimated variance   | 3.092   | 17.779  | 12.732  | 19.428  | 13.415  |
| Sample standard deviation  | 1.689   | 4.074   | 3.416   | 4.220   | 3.519   |
| Estimated standard deviation   | 1.758   | 4.217   | 3.568   | 4.408   | 3.663   |
| Mean absolute deviation  | 1.508   | 3.725   | 2.967   | 3.590   | 2.893   |
| Median absolute deviation  | 1.200   | 4.000   | 2.800   | 3.100   | 2.210   |
| Standard-error   | 0.488   | 1.089   | 1.030   | 1.272   | 1.016   |
| Lower bound Mean CI  | 17.131  | 13.389  | 8.367   | 7.023   | 6.874   |
| Upper bound Mean CI  | 18.869  | 17.224  | 12.067  | 11.593  | 10.495  |
| <i>Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling</i> |         |         |         |         |         |

## Autumn TSS

XLSTAT 7.5.3 - Descriptive statistics - 9/26/2005 at 6:48:39 PM

Quantitative data description

Data: workbook = XLStat Fall.xls / sheet = Autumn by Hour / range = \$AF\$48:\$AJ\$62 / 15 rows and 5 columns

Missing values in &lt;Data&gt; were ignored

Uniform weighting (default)

Confidence interval (%): 95.00

|                              | 0       | 7       | 24      | 48     | 168    |
|------------------------------|---------|---------|---------|--------|--------|
| No. of values used           | 13      | 15      | 12      | 12     | 13     |
| No. of values ignored        | 2       | 0       | 3       | 3      | 2      |
| No. of min. val.             | 1       | 1       | 1       | 1      | 2      |
| % of min. val.               | 7.692   | 6.667   | 8.333   | 8.333  | 15.385 |
| Minimum                      | 49.000  | 29.200  | 1.690   | 0.169  | 0.000  |
| 1st quartile                 | 60.000  | 42.500  | 6.509   | 2.584  | 1.400  |
| Median                       | 73.470  | 54.000  | 10.810  | 8.300  | 3.290  |
| 3rd quartile                 | 82.918  | 67.600  | 15.721  | 11.450 | 5.738  |
| Maximum                      | 93.750  | 76.000  | 18.000  | 17.800 | 7.690  |
| Range                        | 44.750  | 46.800  | 16.310  | 17.631 | 7.690  |
| Sum                          | 932.839 | 808.216 | 130.253 | 95.636 | 43.069 |
| Mean                         | 71.757  | 53.881  | 10.854  | 7.970  | 3.313  |
| Geometric mean               | 70.435  | 52.216  | 9.088   | 4.941  |        |
| Harmonic mean                | 69.065  | 50.486  | 6.865   | 1.460  |        |
| Kurtosis (Pearson)           | -1.283  | -1.119  | -1.716  | -1.390 | -1.369 |
| Skewness (Pearson)           | -0.134  | 0.086   | -0.113  | 0.215  | 0.275  |
| Kurtosis                     | -0.850  | -0.669  | -1.605  | -0.988 | -1.004 |
| Skewness                     | -0.171  | 0.106   | -0.148  | 0.281  | 0.353  |
| CV (standard deviation/mean) | 0.195   | 0.252   | 0.517   | 0.724  | 0.759  |
| Sample variance              | 180.953 | 172.373 | 28.873  | 30.483 | 5.836  |
| Estimated variance           | 196.032 | 184.686 | 31.498  | 33.254 | 6.322  |
| Sample standard deviation    | 13.452  | 13.129  | 5.373   | 5.521  | 2.416  |
| Estimated standard deviation | 14.001  | 13.590  | 5.612   | 5.767  | 2.514  |
| Mean absolute deviation      | 11.198  | 10.676  | 5.077   | 4.789  | 2.036  |
| Median absolute deviation    | 9.470   | 11.500  | 4.826   | 4.276  | 2.266  |
| Standard-error               | 3.883   | 3.509   | 1.620   | 1.665  | 0.697  |
| Lower bound Mean CI          | 63.296  | 46.355  | 7.289   | 4.306  | 1.794  |
| Upper bound Mean CI          | 80.218  | 61.407  | 14.420  | 11.634 | 4.832  |

Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling

## Autumn COD

XLSTAT 7.5.3 - Descriptive statistics - 9/10/2005 at 9:17:05 PM

Quantitative data description

Data: workbook = XLStat Practice.xls / sheet = Autumn by Hour / range = \$AF\$32:\$AJ\$46 / 15 rows and 5 columns

Missing values in &lt;Data&gt; were ignored

Uniform weighting (default)

Confidence interval (%): 95.00

|                              | 0        | 7        | 24      | 48       | 168     |
|------------------------------|----------|----------|---------|----------|---------|
| No. of values used           | 13       | 15       | 12      | 12       | 13      |
| No. of values ignored        | 2        | 0        | 3       | 3        | 2       |
| No. of min. val.             | 1        | 1        | 1       | 1        | 1       |
| % of min. val.               | 7.692    | 6.667    | 8.333   | 8.333    | 7.692   |
| Minimum                      | 272.000  | 140.000  | 47.000  | 12.000   | 32.000  |
| 1st quartile                 | 283.500  | 164.000  | 55.500  | 47.000   | 42.500  |
| Median                       | 297.000  | 256.000  | 68.000  | 67.000   | 48.000  |
| 3rd quartile                 | 310.500  | 292.000  | 81.000  | 93.500   | 60.500  |
| Maximum                      | 439.000  | 306.000  | 112.000 | 142.000  | 86.000  |
| Range                        | 167.000  | 166.000  | 65.000  | 130.000  | 54.000  |
| Sum                          | 3981.000 | 3647.000 | 843.000 | 863.000  | 669.000 |
| Mean                         | 306.231  | 243.133  | 70.250  | 71.917   | 51.462  |
| Geometric mean               | 303.994  | 235.373  | 68.085  | 61.910   | 49.846  |
| Harmonic mean                | 302.137  | 226.546  | 66.105  | 48.594   | 48.379  |
| Kurtosis (Pearson)           | 4.499    | -1.222   | -0.550  | -0.773   | 0.227   |
| Skewness (Pearson)           | 2.279    | -0.726   | 0.698   | 0.412    | 0.915   |
| Kurtosis                     | 9.515    | -0.838   | 0.600   | 0.178    | 1.857   |
| Skewness                     | 2.917    | -0.897   | 0.914   | 0.539    | 1.171   |
| CV (standard deviation/mean) | 0.138    | 0.241    | 0.270   | 0.504    | 0.275   |
| Sample variance              | 1655.254 | 3193.849 | 329.188 | 1205.410 | 184.249 |
| Estimated variance           | 1793.192 | 3421.981 | 359.114 | 1314.992 | 199.603 |
| Sample standard deviation    | 40.685   | 56.514   | 18.144  | 34.719   | 13.574  |
| Estimated standard deviation | 42.346   | 58.498   | 18.950  | 36.263   | 14.128  |
| Mean absolute deviation      | 24.201   | 47.671   | 14.917  | 27.556   | 10.722  |
| Median absolute deviation    | 11.000   | 36.000   | 12.500  | 21.000   | 7.000   |
| Standard-error               | 11.745   | 15.104   | 5.470   | 10.468   | 3.918   |
| Lower bound Mean CI          | 280.641  | 210.738  | 58.210  | 48.876   | 42.924  |
| Upper bound Mean CI          | 331.820  | 275.528  | 82.290  | 94.957   | 59.999  |

Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling

Autumn NH<sub>4</sub><sup>+</sup>

XLSTAT 7.5.3 - Descriptive statistics - 9/10/2005 at 9:39:55 PM

Quantitative data description

Data: workbook = XLStat Practice.xls / sheet = Autumn by Hour / range = \$AF\$64:\$AJ\$78 / 15 rows and 5 columns

Missing values in <Data> were ignored

Uniform weighting (default)

Confidence interval (%): 95.00

|                              | 0       | 7       | 24      | 48      | 168    |
|------------------------------|---------|---------|---------|---------|--------|
| No. of values used           | 13      | 15      | 12      | 12      | 13     |
| No. of values ignored        | 2       | 0       | 3       | 3       | 2      |
| No. of min. val.             | 1       | 1       | 1       | 1       | 1      |
| % of min. val.               | 7.692   | 6.667   | 8.333   | 8.333   | 7.692  |
| Minimum                      | 20.690  | 16.560  | 2.410   | 4.580   | 0.470  |
| 1st quartile                 | 23.280  | 23.350  | 5.761   | 7.128   | 1.582  |
| Median                       | 35.720  | 30.150  | 9.485   | 9.185   | 3.194  |
| 3rd quartile                 | 39.492  | 32.518  | 11.967  | 10.066  | 6.578  |
| Maximum                      | 40.914  | 35.785  | 15.371  | 16.655  | 14.460 |
| Range                        | 20.224  | 19.225  | 12.961  | 12.075  | 13.990 |
| Sum                          | 420.996 | 424.918 | 110.288 | 110.214 | 57.528 |
| Mean                         | 32.384  | 28.328  | 9.191   | 9.185   | 4.425  |
| Geometric mean               | 31.337  | 27.671  | 8.231   | 8.709   | 3.128  |
| Harmonic mean                | 30.244  | 26.924  | 7.091   | 8.249   | 2.094  |
| Kurtosis (Pearson)           | -1.865  | -0.950  | -1.326  | 0.185   | 0.707  |
| Skewness (Pearson)           | -0.339  | -0.706  | -0.008  | 0.752   | 1.271  |
| Kurtosis                     | -1.893  | -0.390  | -0.868  | 1.990   | 2.718  |
| Skewness                     | -0.434  | -0.872  | -0.010  | 0.985   | 1.627  |
| CV (standard deviation/mean) | 0.253   | 0.207   | 0.435   | 0.345   | 0.880  |
| Sample variance              | 62.096  | 32.226  | 14.653  | 9.211   | 14.003 |
| Estimated variance           | 67.271  | 34.527  | 15.985  | 10.048  | 15.170 |
| Sample standard deviation    | 7.880   | 5.677   | 3.828   | 3.035   | 3.742  |
| Estimated standard deviation | 8.202   | 5.876   | 3.998   | 3.170   | 3.895  |
| Mean absolute deviation      | 7.473   | 4.803   | 3.268   | 2.194   | 2.836  |
| Median absolute deviation    | 5.136   | 2.706   | 2.969   | 1.430   | 1.630  |
| Standard-error               | 2.275   | 1.517   | 1.154   | 0.915   | 1.080  |
| Lower bound Mean CI          | 27.428  | 25.074  | 6.650   | 7.170   | 2.072  |
| Upper bound Mean CI          | 37.341  | 31.582  | 11.731  | 11.199  | 6.779  |

Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling

Autumn TKN

XLSTAT 7.5.3 - Descriptive statistics - 9/10/2005 at 9:41:54 PM

Quantitative data description

Data: workbook = XLStat Practice.xls / sheet = Autumn by Hour / range = \$AF\$80:\$AJ\$87 / 8 rows and 5 columns

Uniform weighting (default)

No missing values

Confidence interval (%): 95.00

|                              | 0       | 7       | 24      | 48      | 168    |
|------------------------------|---------|---------|---------|---------|--------|
| No. of values used           | 8       | 8       | 8       | 8       | 8      |
| No. of values ignored        | 0       | 0       | 0       | 0       | 0      |
| No. of min. val.             | 1       | 1       | 1       | 1       | 1      |
| % of min. val.               | 12.500  | 12.500  | 12.500  | 12.500  | 12.500 |
| Minimum                      | 22.030  | 19.100  | 8.060   | 9.300   | 3.300  |
| 1st quartile                 | 49.700  | 42.405  | 11.185  | 11.060  | 4.365  |
| Median                       | 51.455  | 45.385  | 14.750  | 12.735  | 5.025  |
| 3rd quartile                 | 54.600  | 46.620  | 17.460  | 14.880  | 8.745  |
| Maximum                      | 57.500  | 48.800  | 19.620  | 21.130  | 18.730 |
| Range                        | 35.470  | 29.700  | 11.560  | 11.830  | 15.430 |
| Sum                          | 391.040 | 336.720 | 114.470 | 107.780 | 58.300 |
| Mean                         | 48.880  | 42.090  | 14.309  | 13.473  | 7.288  |
| Geometric mean               | 47.213  | 40.676  | 13.754  | 13.068  | 6.205  |
| Harmonic mean                | 44.809  | 38.641  | 13.166  | 12.712  | 5.513  |
| Kurtosis (Pearson)           | 1.205   | 1.211   | -1.517  | -0.535  | 0.252  |
| Skewness (Pearson)           | -1.633  | -1.649  | -0.098  | 0.867   | 1.297  |
| Kurtosis                     | 6.634   | 6.649   | -0.832  | 1.861   | 4.018  |
| Skewness                     | -2.488  | -2.513  | -0.149  | 1.322   | 1.977  |
| CV (standard deviation/mean) | 0.229   | 0.227   | 0.286   | 0.279   | 0.701  |
| Sample variance              | 109.566 | 80.150  | 14.677  | 12.325  | 22.809 |
| Estimated variance           | 125.218 | 91.600  | 16.774  | 14.086  | 26.067 |
| Sample standard deviation    | 10.467  | 8.953   | 3.831   | 3.511   | 4.776  |
| Estimated standard deviation | 11.190  | 9.571   | 4.096   | 3.753   | 5.106  |
| Mean absolute deviation      | 6.713   | 5.983   | 3.124   | 2.651   | 3.589  |
| Median absolute deviation    | 2.760   | 1.880   | 3.460   | 1.675   | 1.400  |
| Standard-error               | 3.956   | 3.384   | 1.448   | 1.327   | 1.805  |
| Lower bound Mean CI          | 39.518  | 34.083  | 10.882  | 10.333  | 3.016  |
| Upper bound Mean CI          | 58.242  | 50.097  | 17.735  | 16.612  | 11.559 |

Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling

Autumn BOD as determined from COD concentration

XLSTAT 7.5.3 - Descriptive statistics - 9/13/2005 at 9:00:47 PM

Quantitative data description

Data: workbook = XLStat Fall.xls / sheet = Autumn by Hour / range = \$AM\$32:\$AQ\$46 / 15 rows and 5 columns

Missing values in <Data> were ignored

Uniform weighting (default)

Confidence interval (%): 95.00

|                              | 0        | 7       | 24      | 48      | 168    |
|------------------------------|----------|---------|---------|---------|--------|
| No. of values used           | 13       | 15      | 12      | 12      | 13     |
| No. of values ignored        | 2        | 0       | 3       | 3       | 2      |
| No. of min. val.             | 1        | 1       | 1       | 1       | 1      |
| % of min. val.               | 7.692    | 6.667   | 8.333   | 8.333   | 7.692  |
| Minimum                      | 198.560  | 18.200  | 6.110   | 1.560   | 4.160  |
| 1st quartile                 | 206.955  | 21.320  | 7.215   | 6.110   | 5.525  |
| Median                       | 216.810  | 33.280  | 8.840   | 8.710   | 6.240  |
| 3rd quartile                 | 226.665  | 37.960  | 10.530  | 12.155  | 7.865  |
| Maximum                      | 320.470  | 39.780  | 14.560  | 18.460  | 11.180 |
| Range                        | 121.910  | 21.580  | 8.450   | 16.900  | 7.020  |
| Sum                          | 2906.130 | 474.110 | 109.590 | 112.190 | 86.970 |
| Mean                         | 223.548  | 31.607  | 9.133   | 9.349   | 6.690  |
| Geometric mean               | 221.916  | 30.599  | 8.851   | 8.048   | 6.480  |
| Harmonic mean                | 220.560  | 29.451  | 8.594   | 6.317   | 6.289  |
| Kurtosis (Pearson)           | 4.499    | -1.222  | -0.550  | -0.773  | 0.227  |
| Skewness (Pearson)           | 2.279    | -0.726  | 0.698   | 0.412   | 0.915  |
| Kurtosis                     | 9.515    | -0.838  | 0.600   | 0.178   | 1.857  |
| Skewness                     | 2.917    | -0.897  | 0.914   | 0.539   | 1.171  |
| CV (standard deviation/mean) | 0.138    | 0.241   | 0.270   | 0.504   | 0.275  |
| Sample variance              | 882.085  | 53.976  | 5.563   | 20.371  | 3.114  |
| Estimated variance           | 955.592  | 57.831  | 6.069   | 22.223  | 3.373  |
| Sample standard deviation    | 29.700   | 7.347   | 2.359   | 4.513   | 1.765  |
| Estimated standard deviation | 30.913   | 7.605   | 2.464   | 4.714   | 1.837  |
| Mean absolute deviation      | 17.667   | 6.197   | 1.939   | 3.582   | 1.394  |
| Median absolute deviation    | 8.030    | 4.680   | 1.625   | 2.730   | 0.910  |
| Standard-error               | 8.574    | 1.964   | 0.711   | 1.361   | 0.509  |
| Lower bound Mean CI          | 204.868  | 27.396  | 7.567   | 6.354   | 5.580  |
| Upper bound Mean CI          | 242.229  | 35.819  | 10.698  | 12.344  | 7.800  |

Note: The standard deviation and confidence interval of the mean are valid only if the sample results from simple random sampling